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PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

I. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE *.

III.

A few special Cryogens and Cryohydrates.

I HAVE, in the first place, to redeem the promise given in § 89, and, by discussing the behaviour as cryogens and cryohydrates of a few peculiar salts, to complete one part of my undertaking.

§ 105. *Chloride of Calcium as a Cryogen.* A. *Crystallized* $CaCl_2+3H_2O$.—The heat liberated when anhydrous $CaCl_2$ is brought into contact with water interferes with, by diminishing, the manifestation of cold due to the proper liquefaction of the salt and of the ice when the two are brought together. Accordingly in experiments with chloride of calcium as a cryogen which are to serve as a guide to the temperature at which the formation of the cryohydrate may be predicted, we may conveniently begin with the crystallized salt. A seasonable fall of snow last winter enabled me to extend my experiments with the chloride of calcium, not only in regard to the relative quantity of the two constituents, but to the relative effects of snow and pounded ice, and to establish conclusively that the two are of quite equal power when used as one element of a cryogen. The crystallized $CaCl_2 + 3\,H_2O$ was finely powdered and placed in weighed quantities on the weighed snow or crushed ice in a beaker, the two being stirred continuously with the thermometer. Under these conditions the lowest temperature is quickly reached.

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* Communicated June 12, 1875.

Table XII.—Column (1) the weight in grammes of the powdered $CaCl_2 + 3\,H_2O$, column (2) the weight in grammes of the powdered ice or snow, columns (3) and (4) the respective percentages of the two, column (5) the temperature.

(1) $CaCl_2+3H_2O$, grammes.	(2) Snow or ice, grammes.	(3) Per cent., $CaCl_2+3H_2O$	(4) Per cent., snow or ice.	(5) Temperature, Centigrade.
100	33 snow	75	25	−21°
100	50 snow	66·6	33·3	−28
94	60 ice	61·5	38·5	−33
* 75	50 snow	60	40	−32
* 75	50 ice	60	40	−32
50	75 snow	40	60	−27
* 50	100 snow	33·3	66·6	−24
* 50	100 ice	33·3	66·6	−24·5

From this, especially from the examples marked *, it appears that snow and ice are of equal value as elements of cryogens, and that the greatest cold is obtained on mixing 38·5 of ice or snow with 61·5 of the crystallized salt. This is the ratio between $CaCl_2\,3\,H_2O$ and $5{\cdot}74\,H_2O$, or $4(CaCl_2\,3\,H_2O)$ and $23\,H_2O$ or $CaCl_2$ and $8{\cdot}74\,H_2O$.

§ 106. B. *Anhydrous* $CaCl_2$ *as Cryogen.*—Freshly fused $CaCl_2$ was finely powdered and mixed with finely crushed ice.

TABLE XIII.—Columns (1) and (2) show the actual quantities, in grammes, taken of $CaCl_2$ and ice respectively; columns (3) and (4) show the percentages; column (5) shows the lowest temperature reached; and the numbers in column (6) show the temperature to which the mixture rose after all the ice was melted in those cases where the proportion of ice was least.

(1) CaCl$_2$, grammes.	(2) Ice, grammes.	(3) CaCl$_2$, per cent.	(4) Ice, per cent.	(5) Lowest temp. Cent.	(6) Rose to temp. Cent.
50	50	50·0	50·0	+33°	
50	75	40·0	60·0	+10 to	+18°
50	90	35·7	64·3	+ 4 ,,	+14
50	95	34·5	65·5	+ 3 ,,	+11
50	100	33·3	66·7	− 2 ,,	+ 9
50	125	28·6	71·4	−10	
33·3	100	25·0	75·0	−13	
25	100	20·0	80·0	−15	
20	100	16·7	83·3	−14·5	
16·6	100	14·2	85·8	−12	
20	140	12·5	87·5	−12	

Here the lowest temperature is reached at the ratio 1 : 4, or about $CaCl_2 + 15\,H_2O$. We must not attach too much importance to the numbers of this Table, because, as before remarked, the liberation of heat when the anhydrous salt dissolves in, or rather combines with water, largely supplies heat for the liquefaction of the solid ice and salt. And accordingly, though the heat-quantity concerned may be deduced from knowledge of the quantity due to such combination and the specific heat of the solution and the heat of liquefaction of the ice, yet the temperature or heat-tension, being a function of the time or rate of liquefaction, cannot be so deduced. The caking of the chloride is also a source of experimental difficulty.

§ 107. *Monohydrated Chloride of Calcium as a Cryogen.*—On baking the terhydrate of chloride of calcium a porous mass is left, which is used for the absorption of water in gases. This, though called anhydrous in commerce, contains about one molecule of water. And the presence of the water is betrayed when the body is used as a cryogen. The chloride, finely powdered, was weighed upon snow or ice and stirred with the thermometer unceasingly. The higher ratios of frozen water were ice, the lower ones were snow; the two are connected together at the 50 per cent. ratios, marked *.

TABLE XIV.

$CaCl_2 + H_2O$, grammes.	Snow or ice, grammes.	$CaCl_2 H_2O$, per cent.	Snow or ice, per cent.	Temperature, Centigrade.
100	33 snow	75	25	+ 5°
100	50 ,,	66·7	33·3	− 4
75	50 ,,	60	40	−10
*50	50 ,,	50	50	−17
*50	50 ice	50	50	−17
50	100 ,,	33·3	66·7	−17
50	150 ,,	25	75	−16
50	200 ,,	20	80	−16
50	300 ,,	14·3	85·7	−16
50	400 ,,	11·1	88·9	−12
50	600 ,,	7·7	92·3	−10

The margin of ratio for minimum temperature is considerable. The minimum temperature itself is intermediate between the minima for $CaCl_2$ and $CaCl_2 + 3 H_2O$.

§ 108. *The Cryohydrate of Chloride of Calcium.*—A solution of $CaCl_2\ 3 H_2O$, saturated at the temperature of the air (10° C.), was cooled to −20° in snow and ice. The mother-liquor was then exposed to the carbonic-acid-and-ether cryogen. The temperature sank to −37° C. under continual separation of a transparent hydrate. At −37° C. an opaque cryohydrate is formed, and the temperature remains constant for a considerable time. The opaque crystals, on being remelted, showed the following composition. By a silver-determination 6·6835 contained 2·3365 of $CaCl_2$. This shows 36·45 of $CaCl_2$, and exhibits the molecular ratio

$$CaCl_2 + 11{\cdot}8\,H_2O.$$

Mixed Salts, as Cryogens and Cryohydrates.

§ 109. Still bearing in mind the problem of sea-water, we may next consider the behaviour of mixtures of soluble salts, both as cryogens and cryohydrates. Even regarding salts as preserving the individuality of their metallic and non-metallic parts when mixed together, there is a variety of recomposition possible. Thus taking the typical salts AX and BY, we may have A=B or X=Y. No double recomposition is possible in either of the latter cases. But there may still be formed double salts in which each metal is engaged with both non-metallic constituents. I suppose that in the present state of chemical knowledge it would be unwise to assert that any double salt is impossible, especially after the evidence which has been so abundantly given above that the body water is virtually pantameric.

On the other hand, remembering the liberal margin of ratio between ice and a salt for the production of the normal or maximum cold, we shall get by examining the temperature of the cryogen of a mixture of salts and the temperature of their common cryohydrate, if they have one, a valuable and indeed unique insight into their molecular relation, in the sense of determining whether double salts or double recomposition ensues. At present I have confined my examination to the various cases of two salts. Of these a few typical examples are taken; and in the first place a pair of salts are examined which differ only in their metals.

§ 110. *Mixed Nitrates of Potassium and Sodium as Cryohydrate.*—The salts were just fused, poured on a slab, crushed while hot, and bottled. The two salts were weighed in monomolecular ratio; namely, of

KNO_3 there were 33·666 grms.
$NaNO_3$ „ 28·333 „

These quantities were mixed, completely dissolved in water, and allowed to evaporate at 13° C. till crystallization began. The mixture was then cooled in an ice-salt cryogen. At about +12° to +10° C. transparent crystals resembling KNO_3 began to form, and continued to do so as the temperature fell. At about −7° an opaque cryohydrate appeared. This went on till −10° C. was reached, when the whole was pasty. At −13° the mass was not yet dry. At −14°·5 it was nearly dry. At −16°·5 to −17° it became perfectly dry. We find then that

The cryohydrate of KNO_3 solidifies at $-\overset{\circ}{2}{\cdot}7$
„ „ $NaNO_3$ „ −17·5
„ „ equiv. mixture „ − 7 to −17°.

Hence it appears that the presence of the nitrate of sodium lowers the temperature at which the cryohydrate of the nitrate of potassium is formed, while the temperature of final solidification is virtually as low as when the nitrate of sodium was alone present.

§ 111. *Mixed Nitrates of Potassium and Sodium as Cryogen.*—The powdered nitrates being mixed in the same proportion as in § 110, namely 11·22 grms. of KNO_3 and 9·44 grms. of $NaNO_3$, and stirred with about 80 grains of crushed ice, gave a temperature of −16°·8. This is clearly again due to the more powerful cryogen $NaNO_3$, which (§ 75) gave −16°·5.

§ 112. *Mixed Chlorides of Potassium and Sodium as Cryohydrate and Cryogen.*—Taking the salts in monomolecular ratio, namely of

KCl taking 18·625
NaCl ,, 14·625

dissolving in water and allowing it to stand until crystallization just began, a solution was obtained which solidified completely at −21° C. On mixing the mixture of the same salts in the same proportion with crushed ice, the resulting temperature was −21°·8. The temperatures in both cases are evidently governed by the action of the NaCl; for

The cryohydrate of	KCl	solidifies at	−11°·4
,, ,,	NaCl	,,	−22
,, ,,	equiv. mixture	,,	−21
Temperature of	KCl	as cryogen	−10·5
,,	NaCl	,,	−22
,,	equiv. mixture	,,	−21

There is so much difficulty attending the accurate separation of sodium and potassium that no method of analysis of them with which I am acquainted is free from the possible error of 2 or 3 per cent. upon the quantity. Accordingly, for the quantitative study of the mixed cryohydrates or cryohydrate of the mixed salts, the following two simple ones were chosen.

§ 113. *Mixed Chlorides of Potassium and Ammonium as Cryohydrates and Cryogens.*

Of NH_4 Cl were taken 13·375 grms.
,, KCl ,, 18·625 ,,

These were dissolved, mixed, and allowed to evaporate till crystallization just began. On cooling, solidification did not begin till −16°·5 or −17°. The temperature remained for a long time at −17°; and when it had reached −18°·8 the whole mass was solid. Two analyses of the remelted last crop of cryohydrate were made. The solution was weighed into a covered Bohemian-glass basin, evaporated at 100° C. to dryness, kept *in vacuo* over sulphuric acid, weighed, gently ignited, and reweighed.

	grms.		grm.			grm.
(*a*)	4·035	of solution gave	0·9505	of total residue	and	0·4890 KCl
(*b*)	5·817	„	1·3725	„	„	0·7005 KCl

So that the percentage compositions were :—

	a.	*b.*	Mean.
KCl . .	12·12	12·04	12·08
NH_4Cl .	11·43	11·55	11·49
H_2O .	76·45	76·41	76·43

The molecular ratios are accordingly

$$KCl=0{\cdot}1608,\ NH_4Cl=0{\cdot}2148,\ \text{and}\ H_2O=4{\cdot}246,$$

or

$$KCl+1{\cdot}33\,NH_4Cl+26{\cdot}4\,H_2O,$$

or

$$3\,KCl+4\,NH_4Cl+79{\cdot}2\,H_2O.$$

Since the water-worth of NH_4Cl is 12·4 and that of KCl is 16·61 (§ 88), we cannot look upon the compound body as a mixture of the two cryohydrates; but we may perhaps regard it as consisting of seven molecules of the cryohydrate of chloride of ammonium in which three molecules of ammonium are replaced by potassium.

The possible precision in the analysis of the mixed chlorides of potassium and ammonium induced me to extend the examination to the intermediate crops of cryohydrates. Accordingly, the dry salts being mixed as before in equivalent ratio, dissolved, concentrated and cooled, five successive crops of cryohydrate were collected as soon as the temperature had sunk to −16°·5, the last being the mother-liquor.

	(1)	(2)	(3)	(4)	(5	(6)
Solution......	6·6090	5·8765	4·0540	6·8210	6·4720	5·0750
Total residue ..	1·4810	1·3445	0·9375	1·5720	1·4960	1·2145
KCl	·7870	0·6760	0·4630	0·7815	0·7410	0·5890

Therefore

KCl:	11·90	11·50	11·54	11·45	11·44	11·60
NH_4Cl	10·50	11·37	11·58	11·59	11·67	12·32
H_2O	77·60	77·23	76·88	76·96	76·89	76·08

Hence it appears that the composition of the successive crops of cryohydrate is nearly unchanged. The later the crop, the poorer is it in water and potassium and the richer in ammonium. And the increase in the ammonium is greater than the decrease in the potassium. The same ratio of the same chlorides, when used as a cryogen, gave −18°. Accordingly

The cryohydrate of KCl solidifies at −11°·4.
" " NH_4Cl " −15
" " equiv. mixture " −17

and

As a cryogen KCl gives −10·5
" NH_4Cl " −16
" equiv. mixture " −18

§ 114. *Mixed Nitrates of Barium and Strontium as Cryohydrates and Cryogens.*

7·05 grms. of $Sr\,2\,NO_3$,

and

8·70 grms. of $Ba\,2\,NO_3$

were dissolved, mixed, and allowed to evaporate to incipient crystallization. At −1°·2 a cryohydrate began to form; and the whole was solid at −4°·3. Employed as a cryogen, the same mixture of salts gave −5°·8. We have therefore

The cryohydrate of $Sr\,2\,NO_3$ solidifies at . −6°
" " $Br\,2\,NO_3$ " . −0·8
" " equiv. mixture solidifies at −4·3

and

As a cryogen $Sr\,2\,NO_3$ gives . . . −6°
" $Ba\,2\,NO_3$ " . . . −0·9
" equiv. mixture gives . −5·8

§ 115. *Mixed Chlorides of Barium and Strontium as Cryohydrates and Cryogens.*

6·933 grms. of $BaCl_2$

and

5·283 grms. of $Sr\,Cl_2$,

both salts having been gently ignited, were dissolved, mixed, and evaporated to saturation. On cooling, a large quantity of transparent salt fell out above 0°. At about −10° a cryohydrate began to form, and the whole was nearly solid at $-13°\cdot5$ to $-14°$. A small portion, however, remained liquid to $-18°$.

Mixed with snow, the above salts in the above proportion lowers the temperature to $-16°\cdot7$. Comparing as before,

The cryohydrate of $Sr\,Cl_2$ solidifies at	. .	$-17°$
" " $BaCl_2$ "	. .	-8
" " equiv. mixture solidifies at		-18

and

As a cryogen, $SrCl_2$ gives	. . .	$-17°$
" $BaCl_2$ "	. . .	$-7\cdot2$
" equiv. mixture gives		$-16\cdot7$

As it is almost impossible to separate barium and strontium with very great precision, and as it was highly desirable to compare the relative quantities in the cryohydrate in at least one other case besides that of § 113, I chose in the right place the—

§ 116. *Mixed Sulphates of Sodium and Ammonium as Cryohydrates and Cryogens.*

$6\cdot6$ grms. of $(NH_4)_2\,SO_4$

and

$7\cdot1$ grms. of $Na_2\,SO_4$

were dissolved, mixed, and allowed to evaporate to saturation. On cooling to 0°, acicular crystals were deposited (of sulphate of sodium). At $-4°\cdot5$ a cryohydrate began to form; the whole was solid and dry at $-7°$. On analysis, by evaporation to dryness and subsequent strong heating, the portion last to solidify was found in two specimens to have the following composition:—

	a.	*b.*	Mean.
$(NH_4)_2\,SO_4$.	12·23	12·25	12·24
$Na_2\,SO_4$ . .	4·82	4·86	4·84
H_2O . . .	82·95	82·89	82·92

The molecular ratios are accordingly

$Na_2\,SO_4$	1
$(NH_4)_2\,SO_4$	2·72
H_2O	135·2

or nearly

$$4\,Na_2\,SO_4 + 11(NH_4)_2\,SO_4 + 541\,H_2\,O.$$

As (§ 88) the water-worth of $Na_2 SO_4$ is 165·6, and that of $(NH_4)_2 SO_4$ is 10·2, this cryohydrate can neither be regarded as a substitutive cryohydrate like that suggested in § 113 for the cryohydrate of the chlorides of potassium and ammonium, nor as a simply additive cryohydrate; for the joint water-worth is less than that of the ammonium salt alone. The double sulphate of sodium and ammonium is formed; and this has the specific water-worth of 135·2 or (taking the higher molecule) of 541.

That the two salts are not independent of one another, appears from their joint action as a cryogen; for mixed in the above equivalent ratio and stirred with snow, they give −16°. Comparing the joint with the separate effects,

The cryohydrate of $(NH_4)_2 SO_4$ solidifies at −17°
" " $NaSO_4$ " − 0·7
" " equiv. mixture solidifies at − 7

and

As a cryogen, $(NH_4)_2 SO_4$ gives . −17°·5
" $Na_2 SO_4$ " . − 0·7
" equiv. mixture gives −16

It is manifest that the doubling of the salt is not taking place during the solution of its two constituents when their mixture is a cryogen, but that it takes place when from solution they unite together in partnership with water as a cryohydrate.

§ 117. *Variation of both Constituents* (AX + BY).—The fascinating hypothesis of Berthollet that double decomposition always partially ensues when two such salts as AX and BY are mixed, even when no removal from the chemical field takes place of any of the possible new bodies resulting from the recombination, may be critically approached from the side of the cryohydrates with great profit. Let me put the question in two concrete forms, and indeed in two of the forms which I immediately propose to examine experimentally.

Is a solution consisting of

202 grms. of KNO_3 and 142 grms. of $Na_2 SO_4$

dissolved in water, identical with a solution consisting of

170 grms. of $NaNO_3$ and 174 of K_2SO_4

dissolved in the same amount of water?

If they are identical, does any one of the salts KNO_3, $NaNO_3$, K_2SO_4, Na_2SO_4 exist as such in either solution?

§ 118. *Comparison between a mixture of* $2NaNO_3$ *and* K_2SO_4 *and a mixture of* $2KNO_3$ *and* Na_2SO_4 *as Cryohydrates and Cryogens.*

33·666 grms. of KNO_3

and

23·666 grms. of Na_2SO_4,

both anhydrous, were mixed, dissolved, and evaporated to saturation. This gave solution (1). Again,

28·333 grms. of $NaNO_3$

and

29 grms. of K_2SO_4

were treated in the same way. This gave solution (2). On cooling (1) and (2), they showed the same behaviour throughout and solidified to dryness at $-5°$. And accordingly there is so far nothing in their behaviour to disprove their identity. But this does not show that partial double decomposition has ensued in both cases to produce in each mixture a portion of the original synthetical constituents of the other. On the contrary, a comparison of this experiment with those above discussed (of the form $AX+BX$) goes very far to prove, not that there are four salts in each of the solutions 1 and 2, but that there is none of the original salts in either. For it has appeared that when AX and BX are mixed in solution, the temperature of final solidification is in no case sensibly above the temperature required for the solidification of that constituent whose solidification takes place at the lowest temperature. Now, if in solution (1) or (2) there were nitrate of sodium present, whether original or derived, the final solidification would not take place above $-17°$ instead of $-5°$ as found. The absence of nitrate of sodium argues forcibly for the absence of each of the other single salts. The most rational formula for such a mixture is the most empirical one possible. As we cannot intertwine the symbols into a monogram in three dimensions, I arrange them alphabetically, and denote either of the solutions 1 or 2 by $H_{2n}KN_2NaO_{n+10}S$. I suppose the time will come when it will be held as illogical to consider that KNO_3 exists in a solution of nitre as it would be to regard a circle as a straight line which has been bent round.

§ 119. The same salts as in § 118 were now taken, but not in equivalent quantity; namely

For solution A there were 66 grms. of Na_2SO_4 and 87·72 grms. of KNO_3,
" B " 91 " K_2SO_4 " 85 " $NaNO_3$.

The salts, as before, were mixed, dissolved, evaporated to saturation, and cooled. The solutions being saturated at +12°, were first cooled in ice for an hour. During this, two kinds of crystals separated from each in sensible quantity. On further cooling, the temperature became and remained constant at −5° up to solidification. The last liquid portions of A and B having been removed to separate vessels before final solidification, were examined as far as their proportion of sulphuric acid is concerned.

The mother-liquor of A showed in

2·277 grms.
·4205 grm. of ignited residue,
which gave ·2510 of $BaSO_4$,
showing ·0857 or 20·3 per cent. of SO_3 in residue.

The mother-liquor of B showed in

2·434 grms.
·4320 grm. of residue,
which gave ·2390 " of $BaSO_4$,
showing ·082 or 18·8 per cent. of SO_3 in residue.

§ 120. *Sulphate of Potassium and Choride of Sodium as a Cryohydrate.*—The behaviour of the mixture of these salts also points to the non-existence of either.

8·6 grms. of K_2SO_4,
5·85 " NaCl
$(=K_2SO_4+2NaCl)$

were dissolved, mixed, concentrated to saturation, and cooled. At first granular crystals fell out. A cryohydrate began to form at −6°. The whole was dry at −12°·5, whereas if NaCl had been present it would have required −22°. A mixture in the ratio $K_2SO_4 + NaCl$ behaved in a similar way, but was dry at −10° C.

§ 121. *Sulphate of Potassium and Chloride of Ammonium as a Cryohydrate.*—Similarly to § 120, a mixture in equivalent proportions of K_2SO_4 and NH_4Cl became quite dry at −12°. The salt NH_4Cl alone requires −15°.

§ 122. In the subjoined Table the results in regard to mixtures of salts as cryohydrates and cryogens are compared with the behaviour of their constituents in each capacity.

TABLE XV. Cryohydrates and Cryogens of equivalent mixtures of two salts.

Mixed salts.		Temperature of solidification of each constituent as cryohydrate.		Temperature of final solidification of mixture as cryohydrate.	Temperature as cryogen of mixture.
(*a*)	(*b*)	(*a*)	(*b*)	(*a*+*b*)	(*a*+*b*)
(1) KNO_3	$+NaNO_3$...	−2·6	−17·5	−17	−16·8
(2) KCl	+NaCl......	−11·4	−22·0	−21	−21·8
(3) KCl	$+NH_4Cl$...	−11·4	−15·0	−17	−18
(4) $Ba\,2NO_3$	$+Sr\,2NO_3$..	−0·8	−6·0	−4·3	−5·8
(5) $BaCl_2$	$+SrCl_2$......	−8·0	−17·0	−18	−16·7
(6) $(NH_4)_2SO_4$	$+Na_2SO_4$...	−17·0	−0·7	−7	−16
(7) $2KNO_3$	$+Na_2SO_4$...	−2·6	−0·7	−5	
(8) $2NaNO_3$	$+K_2SO_4$...	−17·5	−1·2	−5	
(9) K_2SO_4	+2NaCl ...	−1·2	−22·0	−12·5	

This Table furnishes examples of the three typical kinds of relationship between the constituent salts and the mixture of them; namely,

(*a*) In (1), (2), (4), (5) there appears to be no relationship between the salts. Thermally, the mixture may be considered as a mean. The salt of lower solidifying temperature prevents the solidification of the cryohydrate of its associate. The latter in its turn prevents the extreme cold being quite reached proper to the former when alone. In these cases the mixture, when used as a cryogen, gives a temperature a little above that of its more deeply depressive constituent. When jointly forming a cryohydrate, the complete solidification takes place at a slightly higher temperature than when the more strongly temperature-depressing constituent is alone. The variations from this may not be beyond the limit of observational error.

(*b*) In (3) and (7) double salts must be formed whose cryohydrates demand a lower temperature for solidification than does either of their constituents.

(*c*) Finally, in (8) and (9) the temperature of complete solidification is far above the solidifying temperature of that constituent whose solidifying temperature as a cryohydrate is lowest, where again (in 9) probably a double salt is formed, having, if our analogy hold, a greater water-worth than NaCl and a lesser one than $K_2 SO_4$.

Very remarkable is (6). Prone as the sulphates are to form double salts, we might indeed expect, as we find, a specific temperature for the cryohydrate. The difference of temperature of $a+b$ (6) when used as a cryogen ($-16°$ C.) and when solidifying as a cryohydrate ($-7°$), a difference of 9° C., has at present its only counterpart in iodide of sodium (§§ 65, 68, 69), which as a cryogen has the temperature $-26°{\cdot}5$, as a cryohydrate $-15°$, a difference of $11°{\cdot}5$. Some chemists may not be unprepared for the suggestion that iodide of sodium may be in solution a double salt. To a few general considerations bearing on this and kindred points I may have to return subsequently. Meanwhile the general conclusion to be drawn from the above experiments is probably this. Nitrates of the alkalies and alkaline earths act together, but not in union (no double salts); chlorides may act in union with one another or with sulphates. Sulphates may act together or with chlorides or even with nitrates. The agreement of the composition of the several crops of cryohydrates of (3) (§ 113), which points to the relation of almost exactly $3KCl + 4 NH_4 Cl$, shows that in the society of solid water these chlorides have mutual equivalents, which, if not in simple relation to their so-called atomic weights, are yet equally definite and constant.

I have again to acknowledge my indebtedness to Mr. R. Cowper, who has been good enough to give me great assistance in the above experiments.

II. *On the Polarization of Electrodes in Water free from Air.* *By* J. A. Fleming, *B.Sc.* (*Lond.*), *F.C.S.*, *Science Master in Cheltenham College.*

In the 'Electrical News' for September 2, 1875, I published a short paper, previously read at the Meeting of the British Association at Bristol, entitled "The Decomposition of an Electrolyte by Magneto-electric Induction." In it experiments were described showing that when an electrolyte (viz. dilute sulphuric acid) flows in a very strong magnetic field, the electromotive force generated by its motion effects the electrolysis of the liquid, such electrolysis being held to be proved by the subsequent polarization of the electrodes. No actual liberation of gases was observed, since the electromotive force brought into play was insufficient to effect free decomposition. At the time it was read Professor H. A. Rowland raised certain doubts as to the correctness of the conclusions drawn; and his remarks were published, appended to my paper, in the 'Electrical News.' As these objections would, if correct, have deprived the experiments entirely of any little interest they might otherwise have had attaching to them, it was obviously necessary to examine them carefully.

Professor Rowland's remarks amounted practically to saying that he thought the electrolyte was not really decomposed, but that the polarization observed was in some way or other due to the presence of dissolved air, and that in air-free liquid the effect would not have been observed, at any rate with the electromotive force (about $\frac{1}{800}$ of a Daniell's cell) which came into play.

To meet these doubts two very definite questions have to be examined.

(i) In air-free water, can platinum electrodes be polarized by very small electromotive forces to the same degree and with the same facility as in ordinary aerated water?

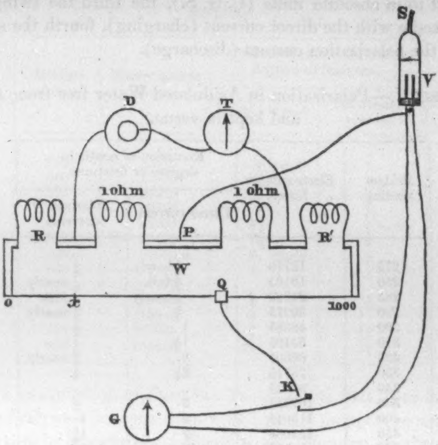
(ii) Is this very feeble polarization really a decomposition of the electrolyte?

If the following facts are held to give an affirmative answer to both the above questions, the objections raised are invalid and may be dismissed.

To test the first point, it was necessary to compare the effect of a small known electromotive force acting through platinum electrodes, first in air free, next in aerated acidulated water, under identical conditions. In the former experiments the electromotive force was generated *in* the liquid by its motion; for my present purpose it was sufficient to act on it by an *external* electromotive force of measurable amount, since it is obvious the results hold good no matter how it is produced. The arrangement consisted of the following parts.

The decomposing cell or voltameter was a glass tube 30 centims. long, 2¼ centims. wide, stopped at one end by an india-rubber stopper, through which passed two platinum wires having welded to them on the interior platinum plates 8 centims. long, 2 centims. wide, placed so as to lie against the walls of the tube. The other end of the tube was connected by a narrow tube with the Sprengel pump. The platinum plates having been rendered chemically clean, the tube was three parts filled with dilute sulphuric acid, which had been previously boiled for six hours so as to expel some of the dissolved air. A vacuum was then made in the voltameter; and the apparatus remained untouched for five days, the pumping being carried on at intervals and continued during the experiments.

To obtain a small electromotive force a well-known method was made use of. A Wheatstone's bridge had its branches filled up with previously measured resistances, and the other connexions made as in the figure (p. 17). Between the points P and Q any small difference of potentials can be produced whose value is known when the distance xQ of the block from the point of equilibrium x is known. The galvanometer employed was a very sensitive mirror-galvanometer, with short needle and a long suspending fibre. The image of a fine wire across the slit was reflected on to a scale in the usual way, and the image viewed through a telescope placed behind the galvanometer. By this means it was found possible to detect and read deflections of the needle amounting only to $\frac{1}{16}$ of a degree with great ease. With this delicate arrangement it was a matter of great difficulty to get the platinum plates perfectly neutral. The last traces of polarization from previous experiments subsided with extreme slowness. The following operations were then performed :—



W.	Wheatstone's bridge.
D.	Daniell's cell.
T.	Tangent-galvanometer.
V.	Voltameter.
G.	Mirror-galvanoscope.
K.	Key.
S.	Tube to Sprengel pump.

(i) The electrodes were made perfectly neutral.

(ii) The galvanometer excluded from the circuit, and a direct current sent through the decomposing-cell for one minute.

(iii) The polarization measured by the swing made by the galvanometer-needle when the electrodes were suddenly connected with it.

(iv) The swing or excursion made by the needle when the same direct current was started through the cell and galvanometer in one circuit, previously bringing the platinum plates to a neutral condition.

The first column in the subjoined Table gives the bridge-reading, the second the electromotive force which this is equivalent to in absolute units (C. G. S.), the third the swing of the needle with the direct current (charging), fourth the same with the polarization current (discharge).

TABLE I.—Polarization in Acidulated Water free from Air and kept *in vacuo*.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization current.
		°	°
275	12110	$\frac{1}{2}$ barely.	$\frac{1}{8}$
280	18165	$\frac{1}{2}$ full.	$\frac{1}{4}$ nearly.
285	24220	$\frac{3}{4}$ nearly.	$\frac{1}{4}$ full.
290	30275	$\frac{3}{4}$	$\frac{1}{2}$ nearly.
300	42385	1	$\frac{1}{2}$
310	54495	$1\frac{1}{2}$	$\frac{1}{2}$
320	66605	2	$\frac{5}{8}$ nearly.
330	78715	$2\frac{1}{4}$	$\frac{5}{8}$
340	90825	…	…
350	102935	3	$\frac{3}{4}$
400	115045	5	1
450	224035	7	$1\frac{3}{4}$
500	284585	10	$2\frac{1}{2}$

Since a Daniell's cell is about 100,000,000 units in electromotive force, the above Table shows that, with the galvanometer employed, the least electromotive force which, acting for one minute under these circumstances on platinum plates of 16·39 centims. surface, would leave a detectable polarization, was about $\frac{1}{8000}$ of a Daniell's cell.

The observations having been repeated several times with the same results, the dilute acid was then removed, and thoroughly aerated by shaking it up with air under pressure, and by bubbling air through it for some time. This aerated water was then returned to the voltameter, all other arrangements remaining the same, and the same observations repeated in this case as in the last. The results are appended.

TABLE II.—Polarization in Acidulated Water thoroughly well aerated.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization current.
		°	°
275	12110	$\frac{1}{2}$ barely.	$\frac{1}{8}$
280	18165	$\frac{1}{2}$	$\frac{1}{8}$
285	24220	$\frac{5}{8}$	$\frac{1}{4}$ barely.
290	30275	$\frac{7}{8}$	$\frac{1}{4}$
300	42385	$1\frac{1}{4}$	$\frac{1}{2}$ barely.
310	54495	$1\frac{1}{2}$	$\frac{1}{2}$
320	66605	2 barely.	$\frac{5}{8}$
330	78715	2	$\frac{3}{4}$ barely.
340	90825	...	...
350	102935	3	$\frac{3}{4}$
400	115045	5	1
450	224035	7	$1\frac{1}{2}$
500	281585	10	$2\frac{3}{4}$

An examination of these two Tables shows that there is very little difference between them which cannot properly be ascribed to errors in observation. There is *no* difference in the minimum electromotive force which could give in each case a visible polarization with the galvanometer employed. But now there was one very striking difference between the two sets of experiments, not shown in the Tables, viz. the time required after each experiment for the polarization to subside. In the case of the aerated water, the polarization disappears *very much* more quickly when the plates are short, circuited than in the case of the air-free water. With this latter it was most troublesome to get rid of the last traces, even with the smallest polarizing currents. This has been previously noticed and explained by Helmholtz *. It is, however, a point not involved in our present considerations.

A consideration of these observations leads apparently to the conclusion that the presence of air in the water has no effect in creating or assisting the polarization of the electrodes under a feeble electromotive force (it is difficult to see any reason why it should), although it has a great effect in removing it when once formed. The process called by Helmholtz *electrolytic convection*, and in which dissolved air is essential, is the consequence and not the cause of polarization.

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* Phil. Mag. [IV.] vol. xlvii. p. 152, Dr. Helmholtz "On Galvanic Polarization in Liquids free from Gas."

It is not true that it requires any definite electromotive force to begin to polarize electrodes in air-free water; any electromotive force, however small, will do it. Its detection is only a question of a sufficiently delicate galvanometer; and we may therefore say that any electromotive force, however feeble, acting on platinum electrodes, builds up a corresponding amount of polarization equally in air-free as in aerated water. But no liberation of free gas is possible under these circumstances, until the external electromotive force just exceeds the counter-electromotive force of the electrodes when polarized to their fullest extent.

With regard to the second question, whether polarization, however small, means literal chemical decomposition, I am not aware that it has ever been called into questiom. There is abundant evidence to show that it is not a mere physical state of the chemically unaltered electrolyte, but that there is *something* deposited on the electrodes which can only be the products, primary or secondary, of electrolysis. Although a voltameter charged by a weak electromotive force resembles very closely a condenser, yet there is something very different between the state of strain or electrical displacement in a condenser's dielectric and the electrolyte after having had a current passed through it.

That even very feeble polarization does really in every case consist in the deposition of products of an unseen electrolysis in or on the electrodes receives support, in addition to many other facts, from the following :—Platinum plates were placed in the inside of a vertical glass tube, and made to communicate with the outside by wires sealed through the glass. The tube was so arranged that dilute acid could be made to flow down through the tube from a reservoir, without the plates being ever exposed to air. The tube being full of acid, the platinum plates were now polarized feebly. If the acid was allowed to flow out *slowly*, so as to gradually replace the liquid which was between the plates when polarized by other fresh acid, the plates gave, on discharge, a nearly equal current to that which they would have given if no replacement had been made; but if the liquid was made to rush down *violently* and then stopped, little or no polarization was found, provided the plates had been only slightly polarized. If the plates were defended by strips of cloth laid over them, no such removal was effected by the liquid rushing down. This all seems to indicate that there is something on the plates which can be *wiped off* mechanically. This can only be the products of electrolysis. This experiment has no analogy in a condenser. These and many other facts seem to point out that polarization is in all cases only unseen electrolysis.

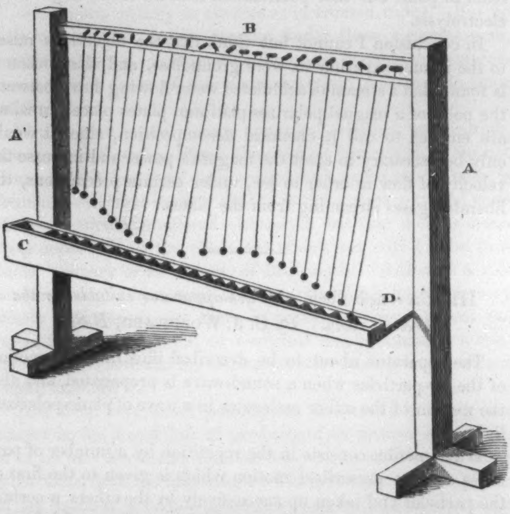
In conclusion I cannot but think that the objections raised to the former experiments were groundless, and that, when it is found that a stream of acidulated water flowing down between the poles of a magnet polarizes platinum plates placed in it, we are entitled to call it chemical decomposition, since it would only be necessary to exalt the magnet's power and increase the velocity of flow in order to see, under certain precautions, the liberated gases streaming from the plates.

III. *On a new Form of Wave-apparatus suitable for the Lecture-room.* *By* C. J. WOODWARD, *B.Sc.**

The apparatus about to be described illustrates the motion of the air-particles when a sound-wave is propagated, and also the motion of the æther molecules in a wave of plane-polarized light.

Wave motion consists in the repetition by a number of particles of some prescribed motion which is given to the first of the particles and taken up successively by the others, a certain interval elapsing between the successive motions. If, for example, we have a number of pendulums of equal length hanging from a beam, but their lower ends supported so that they are out of the vertical, we shall find on releasing one of them, say the left-hand end one, it will commence swinging to and fro; by the time the first pendulum has gone over one fourth of its path release the second, and then after equal intervals the third, fourth, &c., and a wave motion will be produced. If each pendulum was drawn aside in a line at right angles to the beam from which they are suspended, a wave corresponding to a ray of polarized light will be produced; but if each had been drawn aside in the same plane as that of the beam, a wave corresponding to that of a ray of sound would be obtained. We require, then, in order to illustrate these waves, merely a row of pendulums and some arrangement for releasing them in succession.

The apparatus I have used is represented in the figure. A, A are two uprights about 10 feet high, with a crosspiece B fastened firmly to them. At intervals of 3 inches along this crosspiece are inserted violin-pegs, each peg carrying a light string



Plane wave produced by placing the pendulums in the compartments of the box C and releasing them in succession by lowering the box. In the figure the last ball is about leaving the box.

with a heavy ball of 1 inch diameter attached. Before fastening the strings to the violin-pegs, each string is passed through a small hole in the projecting base of the crosspiece, so that the length of the pendulum is determined by the distance of the ball from the base of the crosspiece. C is a light wooden box deeper at one end than at the other, with a number of compartments corresponding to the number of pendulums. The box C is attached at the ends to two radial arms, one of which, D, is seen in the figure. Cords are also attached to C running over pulleys, by which the box C may be raised and lowered. These cords would confuse the figure if introduced; and their action can be easily realized.

Suppose it be wished to illustrate a plane wave. The box C is raised, and the pedulums are placed one in each compartment so that they are all drawn on one side. By means of the cords the box C is gently lowered, when the pendulums are successively released and the wave formed.

To illustrate the sound-wave, the box C is removed from the radial arms and is hung vertically underneath the crosspiece B; one or two of the pendulums (to the left, say) are removed, and the others placed in the compartments as before; only now each pendulum, instead of being drawn from under the crosspiece, lies still underneath, but to the left of the vertical line let fall from each point of support. On now allowing the box to fall slowly, the pendulums are released successively and a wave of condensation and rarefaction is formed.

In conclusion I should acknowledge the assistance of Mr. H. F. Marshall, of Birmingham, who has rendered great service in simplifying the mechanical arrangements of the apparatus.

Birmingham and Midland Institute,
January 1876.

IV. *On some Problems connected with the Flow of Electricity in a Plane.* *By* OLIVER J. LODGE, *B.Sc.*[*]

The following paper may be regarded as a sort of appendix to a paper by Professor G. C. Foster and myself, entitled "On the Flow of Electricity in a uniform plane Conducting Surface," and published in the Philosophical Magazine for May, June, and December 1875 ([IV.] vol. xlix. pp. 385–400 and 453–471, and vol. l. pp. 475–489), in which the known laws of the flow of electricity in an unlimited plane were deduced from the fundamental idea that the effects of any number of poles could be obtained by simple summation of the effects due to each pole separately, without using any mathematics higher than elementary algebra. Several questions arose in the course of the paper which it was not thought advisable to consider then, but some of which seemed to deserve a separate treatment; these are the subjects I propose to develop in the present communication.

§ 1. Imagine a plane sheet, some portions having infinite conducting-power, other portions consisting of ordinary matter, and again other portions possessing infinite resisting-power. The whole extent of any of the infinitely conducting regions will have a uniform potential; and hence the bounding line between any such region and the ordinary matter of the sheet must be an equipotential line. Further, if one defines a line of flow or stream-line as a line across which no electricity passes, the boundary line between the ordinary matter of the sheet and an infinitely resisting region must be a line of flow, for no electricity can possibly get across it. Such a sheet will therefore contain a certain number of flow-lines and a certain number of equipotential lines. Moreover let the potential of any one of the conducting regions be maintained higher than that of some other one, then in general a uniform flow of electricity will take place throughout the whole of the ordinary matter of the sheet, which will therefore contain additional stream-lines and equipotential lines, whose arrangement will depend on the situations and potentials of the various non-material regions.

Some general properties of the equipotential and stream-lines were pointed out in § 35 of the paper referred to. One of these properties is, of course, that the lines of one system cut the lines of the other orthogonally; a more general statement is the following. If a flow-line passes n times through a given point of the sheet, it will form at that point an equiangular pencil whose $2n$ rays meet each other at an angle $\frac{\pi}{n}$; and if no pole exists at the meeting-point it will be a point of no flow, and an equipotential line will also pass n times through the same point, making an equiangular pencil the same in all respects as the former, but turned through an angle of $\frac{\pi}{2n}$, so that its rays bisect the angles of the first pencil. The ordinary orthogonal section is the special case of this when $n=1$. The special case $n=\infty$ is obtained if, in the sheet imagined above, one of the conducting regions touches one of the resisting regions along a line; when this happens, the line separating the two may be regarded indifferently as a stream-line or as an equipotential line.

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[*] Read on the 26th of February and the25th of March, 1876.

There are then two ways of making any given line a stream-line—viz. either by arranging the non-conducting regions so that the line shall bound one of them, or else by arranging the conducting regions and their potentials in such a way that none of the flow of electricity shall take place *across* any portion of the given line. Similarly any line may be made an equipotential line, either by making it bound a region of infinite conductivity, or else by adjusting the potentials and positions of these same regions so that no part of the flow shall take place *along* the given line.

Such a sheet as we have imagined can be approximated to by a piece of tinfoil cut to any shape, with any number of holes in it, and having on its surface blocks of clean copper which are connected with a thermo-pile or other means of maintaining constant difference of potential.

§ 2. The conditions of flow in such a sheet, however, are in general unknown. But if infinitely resisting regions are absent, and if the infinitely conducting regions are reduced to mere points of infinite potential, we get the case of an unlimited sheet containing point poles; and in this all the conditions of the flow are completely known for every point of the sheet.

Thus the potential at any point distant $r_1, r_2 \ldots$ from the poles which emit quantities of electricity $q_1, q_2 \ldots$ in unit time, and which tend to produce potentials $\phi_1, \phi_2 \ldots$ at unit distance from themselves, is (§ 33 of the former paper)

$$V = \Sigma\phi - \frac{1}{2\pi\kappa\delta}\Sigma q \log r, \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

where δ is the thickness and κ the specific conductivity of the sheet; and from this expression stream-line equations and resistance expressions follow.

So, then, the problem of finding the flow conditions in any bounded sheet containing point poles will be solved if we can imitate the electrical boundary conditions in an unlimited sheet by introducing extra point poles into it. These additional poles are called images in the boundary, because they produce the same effect in the given portion of the sheet as the boundaries themselves produced—just as the illumination inside a mirror-walled room containing candles would be imitated in unlimited space by placing extra candles at all the points occupied by the images of the original candles in the mirrors.

Images in rectilinear boundaries.

§ 3. Now let it be required to cause a given *straight* line in an infinite sheet of tinfoil to be a stream-line. All that is necessary is to arrange all the blocks of copper in the sheet symmetrically with respect to this line; that is to say, they must either be placed symmetrically upon the line, or they must be placed in pairs one on each side of it and at equal distances from it. It is usual to express this fact in the inverse way thus:—The image of a pole in a straight flow-line is a pole of the same size, shape, and strength, and situated at an equal distance on the other side of the line so as to be opposite to the first pole.

Again, in order to make a given straight line into an equipotential line, the blocks must be arranged skew-symmetrically with respect to the line—that is to say, in pairs one on each side of it and at equal distances from it, but the sign of one of the constituents of each pair must be opposite to that of the other. This fact is expressed thus:—The image of a pole in a straight equipotential line is a pole of the same size, shape, and numerical strength, but of opposite sign, and situated at an equal distance on the other side of the line.

Hence, if we have given a sheet of tinfoil bounded by a straight edge (*i. e.* by a straight flow-line) and with any distribution of poles in it whatever, and we wish to find the distribution of poles which would make that straight line a flow-line in the unlimited sheet, we have only to regard the line as a plane mirror whose silvered face is turned towards the sheet, and the optical images of the several poles will give the distribution required. The distribution of poles will be obtained in the same way if the boundary is a straight band of copper (*i. e.* an equipotential line); but in this case the sign of every image must be reversed.

§ 4. Now take a sheet bounded by two straight flow-lines intersecting one another at any angle θ: every pole in such a sheet will be reflected backwards and forwards between the two edges according to optical laws; and hence it should have a finite series of images lying on a circle and agreeing with those in the kaleidoscope, the reflection coming to an end as soon as a couple of images fall in the space which is behind both mirrors. But here arises a difficulty. When θ is a submultiple of π, the last couple of images coincide and the whole set is symmetrical with respect to both the straight lines, as is required. But if θ is not a submultiple of π, all that happens in the case of the kaleidoscope is that the last two images separate, the apparent number of images being simply increased by 1. But now the images are not arranged symmetrically with respect to *both* the straight lines, and hence they cannot both be flow-lines. In order to obtain symmetry, it is necessary to continue the reflecting process as if the back of the mirrors were silvered as well as the front; and in that case, of course, the number of images becomes infinite. But then some of these infinite images will fall inside the angle θ (that is, will come into the sheet itself), which will be inconsistent with the given distribution of poles in the sheet. Hence it appears to be impossible for the uniform infinite sheet to contain two straight flow-lines which enclose any angle but a submultiple of π, unless the poles are put infinitely close together, forming a complete circular ring whose centre is at the intersection of the two lines; and in this case *every* straight line drawn in the sheet from this centre is a flow-line.

Another way of expressing the facts is to say that both sides of *every* flow-line are to be regarded as mirrors, and its images as always infinite in number though often coincident with one another, and that the problem of reducing the bounded case to that of the infinite sheet becomes impossible whenever the images reflected back into the sheet itself do not coincide both in sign and position with the images already there. Similar statements are true of the images in a pair of intersecting equipotential lines.

Another distinction between optical and electrical reflection is, that when two optical images coincide their light-emitting powers are added, but, in the electrical case, coincidence of one image with another does not increase its strength. These differences appear to forbid our imagining that there is any physical meaning in electrical reflection at boundaries analogous to the physical reflection of the waves of light in a mirror.

§ 5. Consider now the images of a point inside a polygon of n sides. We have seen that, without silvering both faces of the boundaries and thereby introducing an unconscionable number of images, some of them *real*, we can only treat angles that are submultiples of π by the method of images. Hence obtuse angles less than π are not allowable. This condition at once excludes all polygons of more than four sides; for as the largest interior angle of a polygon of n sides cannot be less than $\frac{n-2}{n}\pi$, and as it must be less than or equal to $\frac{\pi}{2}$, it is necessary that n shall be equal to or less than 4. And if $n=4$, the polygon must be equiangular, that is, must be a rectangle. If $n=3$, the triangles whose angles are submultiples of π are the equiangular, the isosceles right angled, and the one whose angles are 90°, 60°, and 30°. The pseudo-triangle whose angles are 90°, 90°, and 0° is also a possible case, and is treated below as a special case of the circular sector.

I have not mentioned the case when π itself is one of the angles of a polygon, because this merely reduces the polygon to one of $n-1$ sides; but there is the case of the equiangular polygon with all its angles π, viz. the circle, about which a little shall be said later.

The images of a point in a rectangle occur in groups of four surrounding the vertices of rectangles whose linear dimensions are twice those of the original one, and which cover all the plane.

The images of a point in an equilateral triangle occur in groups of six surrounding the vertices of triangles $\sqrt{3}$ times the linear dimensions of the original one, and covering all the plane.

Application of images to certain cases of bounded plates.

§ 6. Now although the potential of any point is really determined by (A), § 2, as soon as we know the positions of all the images in the sheet, the expression is not in a practicable form; and it would not in the majority of cases be readily possible to bring it to such a form. The way to proceed in such cases is to consider what is required of the potential, and then to write down a function of $x+iy$,

$$\mathrm{W} = \mathrm{V} + \mathrm{U}i,$$

such that the real part satisfies all the conditions required of the potential function, viz. to remain together with its derivatives continuous and finite all over the sheet except at the poles and their images, where it is to become infinite like $q \log r$, to fulfil certain given conditions at the boundary, and to satisfy the equation

$$\frac{d^2\mathrm{V}}{dx^2} + \frac{d^2\mathrm{V}}{d^2} = 0.$$

This being done, V = const. will represent the equipotential lines, and U = const. the stream-lines, and the components $\frac{d\mathrm{V}}{dx}, \frac{d\mathrm{V}}{dy}$ of the flow at any point can be obtained. In this way Dr. E. Jochmann* has expressed all the conditions of the flow in a *rectangle*, bounded either by stream-lines or by equipotential lines, or by both.

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* "Ueber einige Aufgaben, welche die Theorie des logarithmischen Potentials und den Durchgang eines constanten elektrischen Stroms durch eine Ebene betreffen," von Dr. E. Jochmann in Berlin. Schlömilch, *Zeitschrift für Mathematik*, 1865, p. 48.

§ 7. But though the potential expression (A) is often of impracticable form, the expression for the resistance of a conductor, which follows from it, is simpler, and admits of being reduced to a useful form with much ease in many cases. Expressions so obtained may serve to verify the results of more abstruse and general processes; but the principal reason for entering into the subject is that the expressions themselves and several of the continued products which lead to them seem to be of some little mathematical interest.

Resistance of some rectilinear figures to the current flowing between two small circular electrodes.

§ 8. Let us first remind ourselves how the general resistance-expression is obtained. Given an infinite sheet with any number k of *equal* sources $A_1, A_2, \ldots A_k$ and the same number of equal sinks $B_1, B_2, \ldots B_k$ in it, the resistance between the two equipotential lines which pass through any two fixed points P and Q is given by Ohm's law as

$$R_{PQ}=\frac{V_P-V_Q}{kq},$$

where V_P stands for the actual potential at the point P, and kq stands for the whole strength of current flowing in the sheet—that is to say, for the quantity of electricity emitted by each source per second, multiplied by the number of sources. Now (A) gives as the potential at any point P

$$V_P=-\frac{q}{2\pi\kappa\delta}\log\frac{A_1P\,.\,A_2P\ldots}{B_1P\,.\,B_2P\,.\,.}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)'$$

hence

$$R_{PQ}=\frac{1}{2k\pi\kappa\delta}\log\left\{\frac{A_1Q\,.\,A_2Q\ldots}{B_1Q\,.\,B_2Q\ldots}\,.\,\frac{B_1P\,.\,B_2P\ldots}{A_1P\,.\,A_2P\ldots}\right\}. \quad . \quad (B)$$

And these expressions are perfectly general; for unequal poles may be regarded as aggregations of equal ones, and the number of sinks *must always* be equal to the number of sources, although some of them may often be at infinity.

Now we know that the equipotential lines of high potential break up into k portions which ultimately become little circles, one surrounding each source. Similarly the lines of low potential surround the sinks. Take the point P on the circumference of one of these little circles (radius ρ_1), that surrounding the source A say (omitting its suffix); and take the point Q on a circle (radius ρ_2) surrounding the sink B. Then the resistance between the two small circular electrodes A and B is k times as much as that offered by the sheet to the $2k$ poles, or

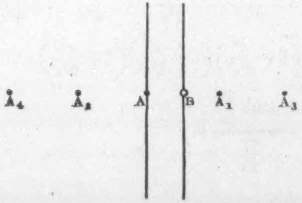
$$R_{AB}=\frac{1}{2\pi\kappa\delta}\log\left\{\frac{AB\,.\,A_1B\,.\,A_2B\ldots}{\rho_1\,.\,A_1A\,.\,A_2A\ldots}\cdot\frac{BA\,.\,B_1A\,.\,B_2A\ldots}{\rho_2\,.\,B_1B\,.\,B_2B\ldots}\right\},(\alpha)$$

where the higher powers of ρ_1 and ρ_2 are neglected. Since they are both small there is no necessity to distinguish them, and ρ^2 may be written for their product. Moreover in very many cases the sources and sinks will be similarly arranged; so that the two fractions which are multiplied together inside the brackets of (α) are equal to one another, and we may then use the simplified expression

$$R_{AB}=\frac{1}{\pi\kappa\delta}\log\left(\frac{AB\,.\,A_1B\,.\,A_2B\ldots}{\rho\,.\,A_1A\,.\,A_2A\ldots}\right). \quad . \quad . \quad (\beta)$$

§ 9. Before proceeding to apply the image theory and this expression to the general case of a two-sided figure, it will be well to consider a special case or two,—and first the very simple case of a parallel-sided strip of breadth s, with the two poles, A and B, one on each side of the strip and opposite to one another (fig. 1).

Fig. 1.



A will be reflected in the opposite side, its image A_1 being at a distance s from that side and from B; then A_1 will be reflected, its image A_2 being $2s$ distant from A and $3s$ from B; then A_2 will be reflected, and so on. The images of B will evidently be similarly arranged to those of A *mutatis mutandis*;

so we may use the second of the resistance-formulæ

$$\mathrm{R}=\frac{2}{\pi\kappa\delta}\log\frac{\mathrm{AB}\,.\,\mathrm{A_1B}\ldots}{\rho\,.\,\mathrm{A_1A}\ldots},$$

doubling it because the poles are only halfway on the sheet (see below, § 22). Now

$$\begin{array}{ll} \mathrm{AB}=\mathrm{A_1B}=s, & \mathrm{A_1A}=\mathrm{A_2A}=2s, \\ \mathrm{A_2B}=\mathrm{A_3B}=3s, & \mathrm{A_3A}=\mathrm{A_4A}=4s, \\ \mathrm{A_4B}=\mathrm{A_5B}=5s, & \ldots\ldots \\ \ldots\ldots & \end{array}$$

Hence the above product becomes

$$\frac{s}{\rho}\cdot\frac{1\,.\,3\,.\,3\,.\,5\,.\,5\,.\,7\ldots}{2\,.\,2\,.\,4\,.\,4\,.\,6\,.\,6\ldots},$$

which equals $\frac{s}{\rho}\cdot\frac{2}{\pi}$.

Therefore

$$\mathrm{R}=\frac{2}{\pi\kappa\delta}\log\frac{2s}{\pi\rho}.\quad.\quad.\quad.\quad.\quad.\qquad(1)$$

§ 10. One more special case of the infinite strip I will take, because a constantly occurring product occurs here in its simplest form. Let the two poles be both on the same side of the strip and at a distance c from one another. The images of A are just as before, and the product $\frac{\mathrm{AB}}{\rho}\cdot\frac{\mathrm{A_1B}}{\mathrm{A_1A}}\cdot\frac{\mathrm{A_2B}}{\mathrm{A_2A}}\ldots$ equals

$$\left\{\frac{c^2}{\rho^2}\cdot\frac{2^2s^2+c^2}{2^2s^2}\cdot\frac{2^2s^2+c^2}{2^2s^2}\cdot\frac{4^2s^2+c^2}{4^2s^2}\cdot\frac{4^2s^2+c^2}{4^2s^2}\ldots\right\}^{\frac{1}{2}}.$$

$$=\frac{c}{\rho}\left(1+\frac{c^2}{2^2s^2}\right)\left(1+\frac{c^2}{4^2s^2}\right)\left(1+\frac{c^2}{6^2s^2}\right)\ldots$$

$$=\frac{c}{\rho}\cdot\frac{\sinh\frac{\pi c}{2s}}{\frac{\pi c}{2s}}\,*.$$

---

* Here and elsewhere sinh x may be considered merely an abbreviation for $\frac{e^x-e^{-x}}{2}$, or as equal to $\frac{1}{i}\sin ix$. Similarly

$$\cosh x=\frac{e^x+e^{-x}}{2},\text{ or }=\cos ix,$$

and

$$\tanh x=\frac{e^x-e^{-x}}{e^x+e^{-x}}=\frac{1}{i}\tan ix,$$

Therefore

$$R=\frac{2}{\pi\kappa\delta}\log\left(\frac{2s}{\pi\rho}\sinh\frac{\pi c}{2s}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Similarly, if we had taken the poles one on each side of the strip, but, instead of opposite each other as at first, at a distance c from one another measured parallel to the sides of the strip, we should have obtained

$$R=\frac{2}{\pi\kappa\delta}\log\left(\frac{2s}{\pi\rho}\cosh\frac{\pi c}{2s}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

If s be made infinite, (2) becomes $\frac{2}{\pi\kappa\delta}\log\frac{c}{\rho}$, which is the correct expression for the case of two poles on the edge of half an infinite sheet. If s is small, (2) and (3) become equal; and if $s=\rho$, they reduce to $R=\frac{c}{\kappa\rho\delta}$ (neglecting the small term $-\frac{2}{\pi\kappa\delta}\log\pi$), which is right for the resistance of a wire or thin strip of sectional area $\rho\delta$ and length c. The presence of the term neglected in comparison with a term which has ρ in its denominator, can be accounted for by remembering that the electrodes are not exactly straight bars at a distance c, but quadrants of small circles whose *centres* are distant c from one another.

§ 11. We may also consider one special case of the infinite "wedge" or *irregular* two-sided polygon. Let the two poles be one on each side of the wedge at the same distance r from its angle O, and call this angle $\theta=\frac{\pi}{n}$ (n integer). The images of A will lie on a circle with centre O (fig. 2), as in the kaleidoscope.

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where $i=\sqrt{-1}$. It is useful to remember that

$$\cosh^2 x-\sinh^2 x=1,$$

that

$$\sinh 0=\tanh 0=\sin 0=0,$$

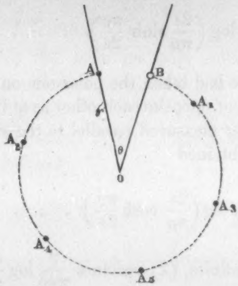
that

$$\cosh 0=\tanh\infty=1,$$

and that

$$\sinh\infty=\cosh\infty=\tfrac{1}{2}e^{\infty}$$

Fig. 2.



Then

$$AB=A_1B=2r\sin\frac{\theta}{2},\qquad A_1A=A_2A=2r\sin\frac{2\theta}{2},$$

$$A_2B=A_3B=2r\sin\frac{3\theta}{2},\qquad A_3A=A_4A=2r\sin\frac{4\theta}{2},$$

$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\qquad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\ ;$$

so the product which occurs in (β) equals

$$\frac{2r}{\rho}\cdot\frac{\sin^2\frac{\theta}{2}\sin^2\frac{3\theta}{2}\sin^2\frac{5\theta}{2}\dots}{\sin^2\frac{2\theta}{2}\sin^2\frac{4\theta}{2}\sin^2\frac{6\theta}{2}\dots}\left\{\begin{array}{l}\dfrac{\sin^2\frac{n-1}{2}\theta}{\sin^2\frac{n}{2}\theta}\sin\dfrac{n\theta}{2}\text{ when } n \text{ is even,}\\[2ex] \dfrac{\sin^2\frac{n-2}{2}\theta}{\sin^2\frac{n-1}{2}\theta}\sin\dfrac{n\theta}{2}\text{ when } n \text{ is odd.}\end{array}\right.$$

But we know from Trigonometry that

$$\sin\frac{\pi}{2n}\sin\frac{3\pi}{2n}\dots\left\{\begin{array}{l}\sin\dfrac{n-1}{2n}\pi\\[2ex]\sin\dfrac{n-2}{2n}\pi\end{array}\right.=2^{\frac{2}{n-1}},$$

and that

$$\sin\frac{2\pi}{2n}\sin\frac{4\pi}{2n}\dots\left\{\begin{array}{l}\sin\dfrac{n-2}{2n}\pi\\[2ex]\sin\dfrac{n-1}{2n}\pi\end{array}\right.=2^{\frac{2}{n-1}}\sqrt{n},$$

the upper termination to be taken when n is even, the lower when n is odd. Hence the above product equals

$$\frac{2r}{\rho}\cdot\frac{1}{n},$$

and

$$R=\frac{2}{\pi\kappa\delta}\log\frac{2r\theta}{\pi\rho}\text{ or }=\frac{2}{\pi\kappa\delta}\log\frac{2s}{\pi\rho}, \quad . \quad . \quad . \quad (4)$$

if one writes s for the arc subtending θ of the circle whose radius is r.

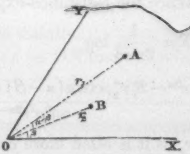
Notice here the close resemblance to (1), becoming identity when $r=\infty$, and also the sort of circular analogy to Wallis's form of $\frac{\pi}{2}$ which one gets by taking arcual instead of linear distances in fig. 2 for the product of (β).

The circle on which all the poles lie is a flow-line by symmetry; and hence the resistance of the sector A O B is twice that of the wedge.

General resistance of a "Wedge," or two-sided polygon, poles any where.

§ 12. If we obtain an expression for the case of two poles A and B, it will be little more than a matter of writing to extend it to any number. Let O X and O Y be the two sides of the wedge, the angle Y O X being $\theta=\frac{\pi}{n}$. Call the distance O A, r_1; and the angle A O X, α (fig. 3); and let (r_2, β) denote the point B. The images of A will lie in pairs on a circle of radius r_1, those of B on a circle of radius r_2; and to find the value of the products which occur in the general expression (α) we may make use of Cotes's (or Demoivre's) property of the circle, which says that, if m points equisect the circumference of a circle of radius r_1, the product of their distances from another point, distant r_2 from the centre of the circle and $\sqrt{(r_1^2-2r_1r_2\cos\phi+r_2^2)}$ from the nearest of the m points, will be equal to

Fig. 3.



$$\sqrt{(r_1^{2m}-2r_1^m r_2^m\cos m\phi+r_2^{2m})}. \quad . \quad . \quad . \quad . \quad (C)$$

To apply this theorem to the present case we must consider the images of A in two sets:—one set including A itself and all its images whose angular distance from it is some multiple of 2θ; the other set containing all the remaining images, which will alternate with those of the first set, and will like them divide the circle into n equal parts. The product of all the distances of the first set from the point B will be given by (C) if we put $m=n=\frac{\pi}{\theta}$ and $\phi=\alpha-\beta$; the product for the second set will only differ in having $\phi=\alpha+\beta$. From the symmetry of the expression, it follows that the product of the distances of the images of B from the point A will be the same as that of the images of A from the point B. Hence the numerator of (α) is determined. As for the denominator, the product of the distances of the second set of images of A from the point A is

$$2r_1^n \sin n\alpha.$$

The product of the first set appears to be zero, since A itself is one of the set; but remembering that the point to which distances are properly measured is not the actual pole A but a point on the circumference of its small electrode (§ 8), we see that the product becomes

$$r_1^n-(r_1-\rho)^n=nr_1^{n-1}\rho,$$

neglecting high powers of ρ. So the whole product of the A's from A is $2n\rho r_1^{2n-1}\sin n\alpha$; similarly the product of the B's from B will be

$$2n\rho r_2^{2n-1}\sin n\beta.$$

Hence the resistance-expression (α) reduces to

$$\mathfrak{R}=\frac{1}{2\pi\kappa\delta}\log$$

$$\frac{\left(r^{2n}-2_1^n r_2^n r\cos n(\alpha-\beta)+r_2^{2n}\right)\left(r^{2n}-2r_1^n r_2^n\cos n(\alpha+\beta)+r_2^{2n}\right)}{4n^2\rho^2 r_1^{2n-1}r_2^{2n-1}\sin n\alpha\,.\,\sin n\beta},\quad(5)$$

or, as it is often more convenient to write it,

$$=\frac{1}{2\pi\kappa\delta}\log$$

$$\left\{\frac{r_1r_2}{\rho^2}\right.\;\frac{\left(\frac{r_1}{r_2}\Big|^n+\frac{r_2}{r_1}\Big|^n-2\cos n\overline{\alpha-\beta}\right)\left(\frac{r_1}{r_2}\Big|^n+\frac{r_2}{r_1}\Big|^n-2\cos n\overline{\alpha+\beta}\right)}{4n^2\sin n\alpha\,.\,\sin n\beta}.\quad(5)'$$

§ 13. A few special cases of this may be recorded.

When $r_1 = r_2$, it becomes

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r}{\rho}\cdot\frac{\cos n\alpha - \cos n\beta}{n\sqrt{(\sin n\alpha\,.\,\sin n\beta)}}\right). \quad . \quad . \quad . \quad (6)$$

If at the same time α be made zero and $\beta = \theta$, we ought to get (4); but we must remember that α is not actually to vanish, it is to become very small and equal to $\frac{\rho}{2r}$, which is a sort of compromise between $\frac{\rho}{r}$, the greatest value it could vanish with, and $\frac{0}{r}$, the least. So putting

$$\alpha = \frac{\rho}{2r}, \quad \beta = \theta - \frac{\rho}{2r},$$

(6) becomes

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r}{n\rho}\cdot\frac{2}{\frac{n\rho}{2r}}\right) = \frac{2}{\pi\kappa\delta}\log\frac{2r}{n\rho},$$

which agrees with (4).

Going back to r_1 and r_2 unequal, let us put both poles on OX—that is, write

$$\alpha = 0 = \frac{\rho}{2r_1} \text{ and } \beta = 0 = \frac{\rho}{2r_2},$$

(5) will become

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{r_1^n - r_2^n}{n^2\rho^2 r_1^{n-1} r_2^{n-1}}\right)^2; \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and this reduces to (2) when r is made infinite.

Similarly if the poles were placed one on OX and the other on OY, we should get

$$\frac{1}{\pi\kappa\delta}\log\frac{(r_1^n + r_2^n)^2}{n^2\rho^2 r_1^{n-1} r_2^{n-1}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and this reduces to (3) when $r_1 = r_2 + c = \infty$, and $\theta = \frac{s}{r} = 0$.

One more case is worth mentioning, viz. when one of the poles, say B, is on the angle of the wedge at O. To give this, $r_2 = \rho$ and (β being any thing between 0 and θ, $n\beta$ will be any thing between 0 and π, say $\frac{\pi}{2}$) $\sin n\beta = 1$, so

$$\mathfrak{R} = \frac{1}{2\pi\kappa\delta} \log\left(\frac{r_1^{2n+1}}{\rho^{2n+1}} \cdot \frac{1}{2n \sin n\alpha}\right). \quad . \quad . \qquad (9)$$

If at the same time A is on OX or OY, this becomes

$$\frac{n+1}{\pi\kappa\delta} \log\left\{\frac{r_1}{\rho} \cdot \left(\frac{\theta}{\pi}\right)^{\frac{1}{n+1}}\right\}. \quad . \quad . \quad . \quad . \qquad (10)'$$

A direct application of Cotes's property and equation (B) to this last case gives us as the perfectly accurate expression

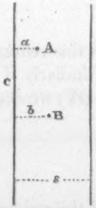
$$\frac{n}{\pi\kappa\delta} \log\left\{\frac{r_1 - \rho_1}{\rho_2} \left(\frac{r_1^n - \rho_2^n}{r_1^n - (r_1 - \rho_1)^n}\right)^{\frac{1}{n}}\right\}, \quad . \quad . \qquad (10)$$

whatever be the size of the electrodes, provided that they be taken of such shape as to fit the equipotential lines passing through the two points P and Q to which distances are measured. Both these points are on the line AB, one of them distant ρ_1 from A, the other ρ_2 from B. This expression will reduce to (10)′ when ρ_1 and ρ_2 are regarded as small quantities of the first order.

§ 14. Although all these expressions are proved only when θ is a submultiple of π, yet by continuity they would seem likely to hold true always. If so, we have expressed the resistance of a Riemann's surface of any number of leaves, but all connected at one branch-point O.

General resistance of a "Strip," or regular two-sided polygon, poles anywhere.

Fig. 4.



§ 15. The strip being a special case of the wedge, its resistance will follow directly from (5)* by making θ vanish. We must substitute

$$s = r_1\theta, \quad a = r_1\alpha, \quad b = r_2\beta, \quad c = r_1 - r_2,$$

and then make $r_1 = r_2 + c$ infinite, keeping c, a, b, s all finite (fig. 4). The substitutions give us

$$\alpha = \frac{a}{s}\theta, \quad \beta = \frac{b}{s}\frac{r_1}{r_2}\theta, \quad n = \frac{\pi}{\theta} = \frac{\pi r_1}{s};$$

so the resistance (5)′ becomes

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[*] It might be objected that when n is made large, higher powers of ρ in the expansion of $(r-\rho)^n$ may not be neglected, as was done in the process of obtaining (5). This would be true if the size of n were merely due to the shutting up of θ with a constant r; but in our present case r is also large, and the expansion is in descending powers of r.

$$\mathfrak{R}=\frac{1}{2\pi\kappa\delta}\log\left\{\frac{s^2}{\pi^2\rho^2}\cdot\frac{\left(\cosh\frac{c}{s}\pi-\cos\frac{a-b}{s}\pi\right)\left(\cosh\frac{c}{s}\pi-\mathrm{co}_{\mathrm{s}}\frac{a+b}{s}\pi\right)}{\sin\frac{a\pi}{s}\sin\frac{b\pi}{s}}\right\}. \quad (11)$$

§ 16. For the case when both poles are at the same distance from the sides of the strip, or $a=b$, this becomes

$$\frac{1}{\pi\kappa\delta}\log\left\{\frac{2s}{\pi\rho}\sinh\frac{\pi c}{2s}\left(\frac{\cosh\frac{c\pi}{s}-\cos\frac{2a\pi}{s}}{1-\cos\frac{2a\pi}{s}}\right)^{\frac{1}{2}}\right\}; \quad . \quad (12)$$

and if they are also both in the middle of the strip, it simplifies to

$$\frac{1}{\pi\kappa\delta}\log\left(\frac{s}{\pi\rho}\sinh\frac{\pi c}{s}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)'$$

which is just half (2), as it ought to be. I write out this particularly, because this case has been already studied by Stefan, and experimentally verified by von Obermayr (*Wien. Akad. Ber.* 1869, vol. lx. part 2. p. 245). Stefan, it seems, wrote the expression he obtained thus (merely altering his letters),

$$\frac{1}{\pi\kappa\delta}\log\frac{s}{2\pi\rho}+\frac{1}{\pi\kappa\delta}\log\left(e^{\frac{\pi c}{s}}-e^{-\frac{\pi c}{s}}\right);$$

and this is identical with (2)$'$.

§ 17. It seems as if expressions like the above might possibly be employed in obtaining the values of certain continued products. Thus to take (12) as an example.

The direct geometrical product for this case, occurring in (β), is the root of

$$\frac{c^2}{\rho^2}.\underline{2a}.\underline{2s-2a}.\underline{2s}.\underline{2s}.\underline{2s+2a}.\underline{4s-2a}.\underline{4s}.\underline{4s}.\underline{4s+2a}.\underline{6s-2a}\ldots,$$

where $\underline{ks\pm 2a}$ is an abbreviation for $1+\frac{c^2}{(ks\pm 2a)^2}$.

Now one portion of this we know (cf. § 10),

$$\left\{\left(1+\frac{c^2}{2^2s^2}\right)\left(1+\frac{c^2}{4^2s^2}\right)\left(1+\frac{c^2}{6^2s^2}\right)\ldots\right\}^2=\left(\frac{2s}{\pi c}\sinh\frac{\pi c}{2s}\right)^2=\mathrm{A}^2 \text{ say};$$

and as $A^2\frac{c^2}{\rho^2}$ equals the square of the rational part of the quantity inside the brackets of (12), it follows that the square of the irrational part is equal to the remaining factors of the above product. It may be written

$$\frac{\cosh\frac{2c\pi}{s}-\cos\frac{2a\pi}{s}}{1-\cos\frac{2a\pi}{s}}=1+\frac{\sinh^2\frac{c\pi}{s}}{\sin^2\frac{a\pi}{s}}=\left(1+\frac{c^2}{a^2}\right)\left(1+\frac{c^2}{(s-a)^2}\right)$$
$$\left(1+\frac{c^2}{(s+a)^2}\right)\left(1+\frac{c^2}{(2s-a)^2}\right)\left(1+\frac{c^2}{(2s+a)^2}\right)\ldots,$$

merely putting s instead of $2s$, and a instead of $2a$.

Whether this result is otherwise obvious or not, it will serve as an example of how new products might sometimes be evaluated from resistance-expressions.

General resistance of a circular sector.

§ 18. The resistance of a circular sector containing two poles A and B will be twice the resistance of a wedge with the same angle, but in which, besides the poles A and B, there also exist poles A′ and B′ at the points inverse to A and B with regard to the circle of which the sector is a part; that is, calling R the radius of the sector, $OA'=\frac{R^2}{r_1}$, $OB'=\frac{R^2}{r_2}$. The expression for the resistance will be (5) plus an additional expression

$$\mathfrak{R}=(5)+\frac{1}{2\pi\kappa\delta}\log$$
$$\frac{\left\{\left(\frac{R^2}{r_1r_2}\right)^n+\left(\frac{r_1r_2}{R^2}\right)^n-2\cos\overline{n\alpha-\beta}\right\}\left\{\left(\frac{R^2}{r_1r_2}\right)^n+\left(\frac{r_1r_2}{R^2}\right)^n-2\cos\overline{n\alpha+\beta}\right\}}{\left(\left(\frac{R}{r_1}\right)^n-\left(\frac{r_1}{R}\right)^n\right)\left(\left(\frac{R}{r_2}\right)^n-\left(\frac{r_2}{R}\right)^n\right)\left(\left(\frac{R}{r_1}\right)^{2n}+\left(\frac{r_1}{R}\right)^{2n}-2\cos 2n\alpha\right)^{\frac{1}{2}}\left(\left(\frac{R}{r_2}\right)^{2n}+\left(\frac{r_2}{R}\right)^{2n}-2\cos 2n\beta\right)^{\frac{1}{2}}}.\quad(13)$$

§ 19. When the angle of the sector vanishes by R becoming infinite, we get the case of a strip bounded towards one end, or what may be called an isosceles triangle whose equal angles are $\frac{\pi}{2}$. The pole A being at a distance c_1 from the base and a from one of the sides, while B is at a distance b from the same side, c_2 from the base, the above expression reduces to

$$R=(11)+\frac{1}{2\pi\kappa\delta}\log\frac{\left(\cosh\frac{c_1+c_2}{s}\pi-\cos\frac{a-b}{s}\pi\right)\left(\cosh\frac{c_1+c_2}{s}\pi-\cos\frac{a+b}{s}\pi\right)}{2\sinh\frac{\pi c_1}{s}\sinh\frac{\pi c_2}{s}\sqrt{\left(\cosh\frac{2\pi c_1}{s}-\cos\frac{2a\pi}{s}\right)}\sqrt{\left(\cosh\frac{2\pi c_2}{s}-\cos\frac{2b\pi}{s}\right)}}, \quad (14)$$

where the c in (11) may be written c_1-c_2 for symmetry.

It may be noticed that the additional quantity in (14) vanishes when c_1 and c_2 are infinite; but becomes the same as (11) when c_1 and c_2 are made small and equal to $\frac{\rho}{2}$; and this is just what it ought to do.

§ 20. The quantity which is added to (11) to give (14) may be called the "effect of the boundary" which limits the strip at one end. If we added a boundary to the other end of the strip also, it would become a rectangle of breadth s and length c_1+c_3 or c_2+c_4; and by adding another quantity to (11) similar to the above, but with c_3 and c_4 instead of c_1 and c_2 (that is, by adding a quantity which approximates to the effect of the new boundary), we should obtain an approximation to the resistance of a rectangle, which is a pretty close one if the c are larger than the s. Such an approximate expression, however, has no particular interest. It is easy to write down the products occurring in (α) for the general case of a rectangle; but their evaluation does not appear to be so simple.

Distribution of potential in a "wedge" containing any number of point poles.

§ 21. All the flow-conditions in a wedge whose angle is $\frac{\pi}{n}$ are determined completely by writing out the particular form assumed by the general expression (A)′, § 8, for this case. The polar coordinates of the sources being (r_1, α), $(r'_1, \alpha')\ldots$, and of the sinks being (r_2, β), $(r'_2, \beta')\ldots$, the potential at any point (r, ϕ) is

$$V=\frac{q}{4\pi\kappa\delta}\log\frac{(r^{2n}-2r^n r_2^n\cos\overline{n\phi-\beta}+r_2^{2n})(r^{2n}-2r^n r_2^n\cos\overline{n\phi+\beta}+r_2^{2n})}{(r^{2n}-2r^n r_1^n\cos\overline{n\phi-\alpha}+r_1^{2n})(r^{2n}-2r^n r_1^n\cos\overline{n\phi+\alpha}+r_1^{2n})} \quad (15)$$

+ similar terms with accented coordinates for every other pair of poles which the sheet may contain.

When the wedge becomes a "strip" of breadth s, the above expression gives, as the potential of any point (x, y),

$$V = \frac{q}{4\pi\kappa\delta}\log \frac{\left(\cosh\frac{y-y_2}{s}\pi - \cos\frac{x-x_2}{s}\pi\right)\left(\cosh\frac{y-y_2}{s}\pi - \cos\frac{x+x_2}{s}\pi\right)}{\left(\cosh\frac{y-y_1}{s}\pi - \cos\frac{x-x_1}{s}\pi\right)\left(\cosh\frac{y-y_1}{s}\pi - \cos\frac{x+x_1}{s}\pi\right)} \quad (16)$$

+ &c.,

where the sources are (x_1, y_1), $(x'_1, y'_1)\ldots$, the sinks (x_2, y_2), $(x'_2, y'_2)\ldots$, and where one side side of the strip is taken as the axis of y.

General form of the resistance-expression for two poles.

§ 22. It is convenient at this point to notice the general form of the resistance-expression for two poles A and B in any bounded plate. It may always be written in the form

$$\frac{c}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}\cdot Q\right), \quad . \quad . \quad . \quad . \quad . \quad (\gamma)$$

where Q is a numerical quantity which depends on the general form of the boundaries of the plate, and on the position of the poles with respect to those boundaries; while c is a number which depends only on that part of the boundary which is infinitely near a pole. As long as the poles are not placed on the edge of the plate, $c=1$ and is unaffected by any change in the boundary; but if either pole is placed on the edge, the angle on which it is placed determines c,—the general law being that if A is on an angle $\frac{\pi}{m}$, and B on an angle $\frac{\pi}{n}$, then $c=m+n$. (When both poles are inside the plate, both angles equal 2π, and therefore $c=1$, as stated above.)

It is unnecessary to prove this rule formally; but it is a consequence of the necessary condition that A and B must be of equal strength in the limited sheet; for this condition requires that if they are on angles $\frac{2\pi}{2m}$ and $\frac{2\pi}{2n}$ respectively, their strengths in the unlimited sheet must be in the ratio of $2m : 2n$, and accordingly the quantity $\frac{AB}{\rho}$ in (α) § 8 will occur to the $2(m+n)$th power.

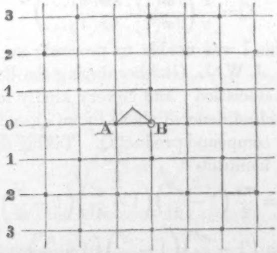
Hence, in the process of finding the resistance of any plane conductor containing two small electrodes, the determination of Q is the only difficulty. We have found it for the general polygon of two sides; let us proceed to find it for a few triangles.

Resistance of an isosceles right-angled triangle. Poles on the equal angles.

§ 23. This case was in reality the first figure with rectilinear boundaries which I attempted. The positions of the images of A are shown in fig. 5; they are on the corners of squares covering all the plane. The images of B will be similarly arranged, every source being surrounded by four sinks.

To determine the value of the product $\left(\frac{AB}{\rho} . Q\right)$ in the resistance-expression (β) (§ 8), take the images in rows, and find the product for each row separately (cf. § 9). Call the line A B, fig. 5, row 0; the two rows one on either side of A B call rows 1; row 2 will be the row next beyond each of these; and so on, the images being evidently symmetrical with respect to the line A B. The whole product Q will then equal $Q_0, Q_1^2, Q_2^2 \ldots$, where Q_x stands for the product of the $\frac{A_x B}{A_x A}$'s in one row x.

Fig. 5.



Images of the pole A in an isosceles right-angled triangle.

From the figure we see that

$$Q_0 = \frac{1\,.\,3\,.\,3\,.\,5\,.\,5\,.\,7\ldots}{2\,.\,2\,.\,4\,.\,4\,.\,6\,.\,6\ldots} \qquad = \frac{2}{\pi} = \frac{1}{\varpi(0)},$$

$$Q_1^2 = \frac{1^2}{1^2+1^2}\cdot\frac{2^2+1^2}{1^2+1^2}\cdot\frac{2^2+1^2}{3^2+1^2}\cdot\frac{4^2+1^2}{3^2+1^2}\cdot\frac{4^2+1^2}{5^2+1^2}\cdots = 1^2.\,\varpi^2(1),$$

$$Q_2^2 = \frac{1^2+2^2}{2^2}\cdot\frac{1^2+2^2}{2^2+2^2}\cdot\frac{3^2+2^2}{2^2+2^2}\cdot\frac{3^2+2^2}{4^2+2^2}\cdots \qquad = \frac{1}{2^2\varpi^2(2)},$$

$$Q_3^2 = \frac{3^2}{1^2+3^2}\cdot\frac{2^2+3^2}{1^2+3^2}\cdot\frac{2^2+3^2}{3^2+3^2}\cdots \qquad = 3^2\varpi^2(3),$$

. . . .

and in general

$$Q_x^{\pm 1} = x\varpi(x),$$

where the index is to be taken positive when x is odd, negative when x is even; and where $\varpi(x)$ stands for the product

$$\frac{2^2+x^2}{1^2+x^2}\cdot\frac{4^2+x^2}{3^2+x^2}\cdot\frac{6^2+x^2}{5^2+x^2}\cdots\frac{1}{\sqrt{(\infty^2+x^2)}},$$

of which Wallis's expression is the particular case when $x=0$.

The entire product Q also shows an evident resemblance to Wallis's form, being

$$Q = \frac{2}{\pi}\left(\frac{1\varpi(1)\,.\,3\varpi(3)\ldots}{2\varpi(2)\,.\,4\varpi(4)\ldots}\right)^2.$$

Further than this I was unable to proceed; so I showed the products to Mr. J. W. L. Glaisher during the Bristol Meeting of the British Association; and he very kindly told me how to evaluate the product denoted above by $\varpi(x)$, and subsequently worked out the compound product Q. Taking the well-known trigonometrical identities

$$\sin\frac{\pi x}{2} = \frac{\pi x}{2}\left(1-\frac{x^2}{2^2}\right)\left(1-\frac{x^2}{4^2}\right)\left(1-\frac{x^2}{6^2}\right)\cdots,$$

$$\cos\frac{\pi x}{2} = \left(1-\frac{x^2}{1^2}\right)\left(1-\frac{x^2}{3^2}\right)\left(1-\frac{x^2}{5^2}\right)\cdots,$$

Mr. Glaisher divided one by the other after putting $x\sqrt{-1}$ for x; he thus obtained

$$\tan\frac{i\pi x}{2} = \frac{i\pi x}{2}\cdot\frac{2^2+x^2}{1^2+x^2}\cdot\frac{4^2+x^2}{3^2+x^2}\cdots\frac{1^2.\,3^2.\,5^2\ldots}{2^2.\,4^2.\,6^2\ldots}$$

$$= \frac{i\pi x}{2}\,.\,\varpi(x)\,.\,\frac{2}{\pi},$$

whence

$$x\varpi(x)=\frac{1}{i}\tan\frac{i\pi x}{2}=\tanh\frac{\pi x}{2}\text{*}.$$

This result gives us

$$\mathrm{Q}=\frac{2}{\pi}\left(\frac{\tanh\frac{\pi}{2}\,.\,\tanh\frac{3\pi}{2}\ldots}{\tanh\frac{2\pi}{2}\,.\,\tanh\frac{4\pi}{2}\ldots}\right)^2.$$

The part inside the brackets may be written

$$\sqrt{\frac{\pi\mathrm{Q}}{2}}=\frac{1-e^{-\pi}}{1+e^{-\pi}}\cdot\frac{1-e^{-3\pi}}{1+e^{-3\pi}}\ldots\frac{1+e^{-2\pi}}{1-e^{-2\pi}}\cdot\frac{1+e^{-4\pi}}{1-e^{-4\pi}}\ldots;$$

and this Mr. Glaisher saw at once was a special case of Jacobi's products; two of which (being those required in this paper) I write down here—

$$\frac{1-q}{1+q}\cdot\frac{1-q^3}{1+q^3}\cdot\frac{1-q^5}{1+q^5}\ldots=k'^{\frac{1}{4}}, \quad . \quad . \quad . \quad . \quad (\delta)$$

$$\frac{1-q^2}{1+q^2}\cdot\frac{1-q^4}{1+q^4}\cdot\frac{1-q^6}{1+q^6}\ldots=\left(\frac{2\sqrt{k'}\mathrm{K}}{\pi}\right)^{\frac{1}{2}}; \quad . \quad (\epsilon)$$

q stands for $e^{-\pi\frac{\mathrm{K}'}{\mathrm{K}}}$, K having its ordinary meaning of

$$\int_0^{\frac{\pi}{2}}\frac{d\theta}{\sqrt{(1-k^2\sin^2\theta)}}.$$

Taking the modulus-angle 45° so that $k=k'=\frac{1}{\sqrt{2}}$ and $\mathrm{K}=\mathrm{K}'=\mathrm{K}_0$ say, and then dividing (δ) by (ε), there results the product required,

$$\sqrt{\frac{\pi\mathrm{Q}}{2}}=\sqrt{\frac{\pi}{2\mathrm{K}_0}}.$$

Hence $\mathrm{Q}=\frac{1}{\mathrm{K}_0}$, and the resistance of a triangle with each electrode on an angle of 45° is

$$\mathrm{R}=\frac{8}{\pi\kappa\delta}\log\left(\frac{\mathrm{AB}}{\rho}\cdot\frac{1}{\mathrm{K}_0}\right). \quad . \quad . \quad . \quad . \quad (17)$$

---

* Mr. Glaisher also obtained an expression for the more general product $\frac{2^n+x^n}{1^n+x^n}\cdot\frac{4^n+x^n}{3^n+x^n}\ldots$, which he has communicated to the Mathematical Society.

The numerical value of K_0 from Legendre's Tables is

$$1{\cdot}854\,074\,677\,301.$$

§ 24. If one writes out (17) in two parts,

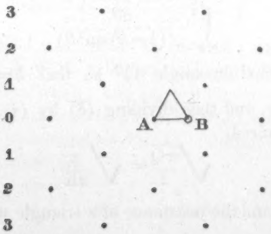
$$\frac{8}{\pi\kappa\delta}\log\frac{\mathrm{AB}}{\rho}-\frac{8}{\pi\kappa\delta}\log\int_0^{\frac{\pi}{2}}\frac{d\theta}{\sqrt{(1-\frac{1}{2}\sin^2\theta)}}, \quad . \quad (17)'$$

the first term is the resistance of a segment of a circle with base AB and with its arc touching the two sides of the triangle at A and B; and the second term may be called the effect of the "coquadrant"* by which the triangle exceeds the segment in area. But one must not imagine that this term expresses the resistance of this figure. The fact is that its resistance cannot be found by any consideration of (17)′, for reasons which shall be stated, § 30, footnote. It is worth while to notice the arrangement of poles and flow-lines which would produce this coquadrant figure in an unlimited sheet; but they will come better later.

Resistance of an equilateral triangle. Poles on two of the angles.

§ 25. The images of A for this case are shown in fig. 6,

Fig. 6.



Images of the pole A in an equilateral triangle.

being on the vertices of equilateral triangles $\sqrt{3}$ times the linear dimensions of the original one. Take the images in rows as before (§ 23), calling the line A B row 0, and find the product Q_x for each row separately.

---

* I call it a *coquadrant* because it is the excess of a square over the quadrant whose radius is a side of the square: more generally the figure enclosed by any circular arc and two tangents might be called a *cosector*; it would be the excess of an isosceles cirquadrilateral over the inscribed sector, and it only differs from a sector in having the equal angles 0° instead of 90°.

$$Q_0 = \frac{2.4.5.7.8.10\ldots}{3.3.6.6.9.9\ldots} = \frac{3\sqrt{3}}{2\pi} = \sqrt{0^2\phi(0)\psi(0)},$$

$$Q_1^2 = \frac{1^2+3}{3^2+3}\cdot\frac{5^2+3}{3^2+3}\cdot\frac{7^2+3}{9^2+3}\cdot\frac{11^2+3}{9^2+3}\cdot\frac{13^2+3}{15^2+3}\cdots = \phi(\sqrt{3}),$$

$$Q_2^2 = \frac{2^2+2^2.3}{2^2.3}\cdot\frac{4^2+2^2.3}{6^2+2^2.3}\cdot\frac{8^2+2^2.3}{6^2+2^2.3}\cdot\frac{10^2+2^2.3}{12^2+2^2.3}\cdots = \psi(2\sqrt{3}),$$

$$Q_3^2 = \frac{1^2+3^2.3}{3^2+3^2.3}\cdot\frac{5^2+3^2.3}{3^2+3^2.3}\cdot\frac{7^2+3^2.3}{9^2+3^2.3}\cdots = \phi(3\sqrt{3}),$$

$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\;;$$

and

$$Q = \frac{3\sqrt{3}}{2\pi}\,\phi(\sqrt{3})\psi(2\sqrt{3})\phi(3\sqrt{3})\psi(4\sqrt{3})\ldots.$$

Now

$$\phi(x) = \frac{1^2+x^2}{3^2+x^2}\cdot\frac{5^2+x^2}{3^2+x^2}\cdot\frac{7^2+x^2}{9^2+x^2}\cdots = \frac{1}{4}\cdot\frac{\cosh\frac{\pi x}{2}}{\cosh^3\frac{\pi x}{6}}$$

$$= \frac{1+3\tanh^2\frac{\pi x}{6}}{4},$$

this result being evident if numerator and denominator are multiplied by

$$3^2+x^2.\,9^2+x^2.\,15^2+x^2\ldots;$$

and similarly

$$\psi(x) = \frac{2^2+x^2}{x^2}\cdot\frac{4^2+x^2}{6^2+x^2}\cdot\frac{8^2+x^2}{6^2+x^2}\cdots = \frac{1}{4}\cdot\frac{\sinh\frac{\pi x}{2}}{\sinh^3\frac{\pi x}{6}}$$

$$= \frac{1+3\coth^2\frac{\pi x}{6}}{4}.$$

Hence

$$Q = \frac{3\sqrt{3}}{2\pi}\cdot\frac{1+3\tanh^2\frac{\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\tanh^2\frac{3\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\tanh^2\frac{5\pi}{2\sqrt{3}}}{4}\cdots$$

$$\times\frac{1+3\coth^2\frac{2\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\coth^2\frac{4\pi}{2\sqrt{3}}}{4}\cdot\frac{1+3\coth^2\frac{6\pi}{2\sqrt{3}}}{4}\cdots$$

This product I sent to Mr. Glaisher; and he returned it reduced to a product of two theta-functions. He proved the two following identities :—

$$P_1 = \frac{1+m\tanh^2\theta}{1+m}\cdot\frac{1+m\tanh^2 3\theta}{1+m}\cdot\frac{1+m\tanh^2 5\theta}{1+m}\ldots$$

$$=\sqrt{\frac{\pi}{2K}}\,\Theta\left(\frac{2Kx}{\pi}\right)$$

and

$$P_2 = \frac{1+m\coth^2 2\theta}{1+m}\cdot\frac{1+m\coth^2 4\theta}{1+m}\cdot\frac{1+m\coth^2 6\theta}{1+m}\ldots$$

$$=\frac{1}{\cos x}\sqrt{\frac{\pi^3}{(2K)^3kk'}}\cdot H\left(\frac{2Kx}{\pi}+K\right),$$

where

$$\cos 2x = \frac{m-1}{m+1} \text{ and } 2\theta = \pi\frac{K'}{K}.$$

In our present case

$$m=3 \text{ and } \theta = \frac{\pi}{2\sqrt{3}};$$

so

$$K=\sqrt{3}K',\ k=\sin 75^\circ, \text{ and } x=\frac{\pi}{6}.$$

Hence

$$P_1=\sqrt{\frac{\pi}{2K}}\,\Theta(\tfrac{1}{3}K),\quad \frac{\sqrt{3}}{2}P_2=\sqrt{\frac{\pi^3}{8K^3kk'}}\,H(\tfrac{2}{3}K),$$

and

$$Q=\frac{3\sqrt{3}}{2\pi}P_1P_2=\frac{3\pi}{4K^2\sqrt{k'}}\Theta(30^\circ)\Theta_1(60^\circ) \text{ (mod. angle } 75^\circ),$$

writing $\Theta_1(x)$ for $\frac{1}{\sqrt{k}}H(x)$.

From the British-Association Tables

$$\log\frac{1}{K^2\sqrt{k'}}=\bar{1}\cdot 4091498986,$$

$$\log\Theta(30^\circ)=\bar{1}\cdot 9223413942,$$

$$\log\Theta_1(60^\circ)=\cdot 0491498189;$$

so

$$\log_{10}Q\quad=\bar{1}\cdot 7528522478,$$

or

$$Q=\frac{1}{1\cdot 76664} \text{ about},$$

and the resistance of the triangle is

$$R=\frac{6}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}.Q\right). \quad . \quad . \quad . \quad . \quad . \quad (18)$$

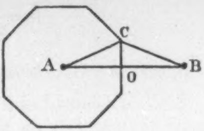
Manner in which the image-method fails for an angle of 120°.

§ 26. We found in § 5 that the only isosceles triangles which could be treated by the method of images were those with the equal angles either 0°, 45°, 60°, 90°, or 180°; and of these all except the first have been already done in the course of this paper (§§ 23, 25, 19, 10), and the first shall be considered in the next section. But suppose we attempted the triangle with equal angles 30°, which is apparently a very simple case; the images of the source A (on one of the equal angles) would be readily placed on the corners of regular hexagons; but they would be symmetrically situated with respect to the middle line of the triangle, and hence when the images of the sink B came to be placed they would coincide with those of A and would blot them all out of the sheet. Or if we overlook this and apply the expression (β) to the images of A, then, because of their symmetry with respect to the triangle, the product Q (§§ 8 & 22) will equal 1; which can be proved to be wrong (§ 27). This failure, caused by the presence of the angle 120°, is one that cannot, even apparently, be got over by silvering both sides of the boundaries (§ 4); for, in order to arrange poles in an unlimited sheet so as to be symmetrical with respect to all three sides of the triangle, it is necessary that one and the same point shall be at the same time both a source and a sink. Dr. Henrici suggests that this is possible if the plane consists of two leaves, and recommends in general, whenever both sides of a boundary have to be silvered and some of the images are *real* (that is, occur in the given plate itself), that these real images be put in another leaf of the plane. It seems just possible that some such contrivance might enable the image-method to be applied to polygons whose angles are not integral submultiples of π.

Empirical formula for the resistance of a general isosceles triangle. Poles on the equal angles.

§ 27. Consider a regular polygon of n sides, with one electrode

Fig. 7.



(radius ρ), A, fig. 7, at its centre, and with its entire periphery maintained at one potential. The resistance R_n of such a polygon to radial flow is evidently something between that of its inscribed and that of its circumscribing circle; in other words,

$$\frac{1}{2\pi\kappa\delta}\log\frac{AO}{\rho} < R_n < \frac{1}{2\pi\kappa\delta}\log\frac{AC}{\rho}.$$

Now the resistance R of the isosceles triangle A B C (fig. 7) equals twice the resistance of the triangle A O C, which again equals $2n$ times the resistance of the polygon. Hence, writing $AC = AO \sec CAO = \frac{1}{2} AB \sec\frac{\pi}{n}$,

$$\frac{2n}{\pi\kappa\delta}\log\frac{AB}{2\rho} < R < \frac{2n}{\pi\kappa\delta}\log\left(\frac{AB}{2\rho}\sec\frac{\pi}{n}\right);$$

or, calling the angle CAO θ, we may write the resistance of any isosceles triangle with equal angles θ,

$$R = \frac{2}{\theta\kappa\delta}\log\left(\frac{AB}{\rho}\,\frac{1}{f(\theta)}\right), \quad . \quad . \quad . \quad . \quad (19)$$

where $f(\theta)$ is something between $2\cos\theta$ and 2. Hence the limit of Q when the angles of the triangle vanish is $\frac{1}{2}$. Moreover when the angles are 30°, $f(\theta)$ must lie between 2 and $\sqrt{3}$; it cannot, therefore, be 1 as the product of images (§ 26) would lead us to believe.

Looking at the few values of $f(\theta)$ which are known, one may notice how nearly they divide the interval allowed to them, $2-2\cos\theta$, in the ratio 1 : 3. The quantity which actually does this is $\frac{3+\cos\theta}{2}$; and this quantity agrees with the known values of $f(\theta)$ to an extent shown in the Table.

θ.	$f(\theta)$.	$\frac{3+\cos\theta}{2}$.
0°	2·0	2·0
45	1·854	1·853
60	1·766	1·75
90	1·57	1·50
180	1·0	1·0

The maximum divergence appears to occur about when $\theta=90°$.

The empirical formula, then,

$$\frac{2}{\theta\kappa\delta}\log\left(\frac{\mathrm{AB}}{\rho}\cdot\frac{2}{3+\cos\theta}\right) \quad . \quad . \quad . \quad . \quad . \qquad (19)'$$

gives the resistance of any isosceles triangle with poles on the equal angles θ with sufficient accuracy for a practical purpose; and it becomes very accurate indeed when the equal angles are small. The value of Q indicated by it for the case $\theta=30°$ is $\frac{1}{1\cdot9330}$; and I venture to think that the real value will be found to differ from this only in the last place of decimals.

The resistance to the flow of electricity from a central electrode of radius ρ to the periphery of a regular polygon of n sides is, to the same degree of approximation as the above,

$$\frac{1}{2\pi\kappa\delta}\log\left(\frac{r}{\rho}\cdot\frac{4}{3+\cos\frac{\pi}{n}}\right), \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

r being the radius of the inscribed circle.

§ 28. And here I would remark that the thickness (δ) of the plate in which the flow takes place has never been limited in any way; so the plate may extend itself into a cylinder of any length, provided the point poles extend themselves into lines at the same time. Also, though we are using the language of dynamic electricity only, yet the resistance obtained applies equally well to heat if we substitute hot and cold bodies for sources and sinks, temperature for potential, and isothermals for equipotential lines. Further, by reason of the analogy between conductivity and inductive capacity, we obtain at the same time the inductive capacity of a dielectric medium exposed to conductors at different potentials which correspond to the poles in the dynamic problem.

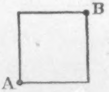
Resistance of some squares and right-angled triangles.

§ 29. The forms assumed by the resistance-expressions (§ 8) for the case of a square plate with the poles in certain definite positions may be recorded, together with the products which lead to them. The resistance seems always to be of the form

$$R=\frac{m+n}{\pi\kappa\delta}\log\left(\frac{AB}{\rho}\cdot\frac{2^{\alpha}}{K_0}\right), \quad . \quad . \quad . \quad . \quad (21)$$

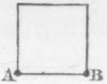
where the poles A and B are on angles $\frac{\pi}{m}$ and $\frac{\pi}{n}$ respectively, and where α takes different values in different cases, and is the only thing which varies. K_0 still stands for the first complete elliptic integral with modulus $\frac{1}{\sqrt{2}}$.

Fig. 8.



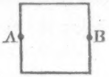
For the case represented in fig. 8 the value of α is zero, because the resistance of such a square is just half that of the right-angled triangle (17) § 23.

Fig. 9.



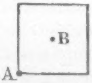
When the poles are as in fig. 9, $\alpha=\frac{1}{4}$; the product in (β) which leads to the result consists of terms $\coth^2\frac{\pi x}{2}$, where x takes the values 2, 4, 6, ...

Fig. 10.



The case of fig. 10 gives us $\alpha=\frac{1}{2}$, the product being $\Pi\left(\coth^2\frac{\pi x}{2}\right)$, with x successively 1, 2, 3, 4, &c.

Fig. 11.



The case of fig. 11, being unsymmetrical in sources and sinks, requires the complete expression (α) § 8; and, because the pole at the corner of the square has to be four times as strong as the other in the infinite sheet, the two factors inside the brackets of (α) occur to different powers; in other words, calling the factors P_1 and P_2, we shall have

$$Q^5=P_1P_2^4.$$

Now P_1, the product referring to the images of the pole at the centre, is the old one whose value is $\frac{1}{K_0}$ (§ 23). But the product for the images of the corner pole will be found to be

$$P_2=\frac{2\sqrt{2}}{\pi}\,\Pi\left(\coth\frac{\pi x}{2}\coth\frac{\pi x}{4}\right)\Pi\left(\frac{\coth\frac{\pi x'}{2}}{\coth\frac{\pi x'}{4}}\right),$$

where x is to take the successive values 4, 8, 12, ..., and x' the values 2, 6, 10, ...

Writing this product P_2 in the form

$$\frac{2\sqrt{2}}{\pi}\cdot\frac{\tanh\frac{\pi}{2}\,.\,\tanh\frac{3\pi}{2}\ldots}{\tanh\frac{2\pi}{2}\,.\,\tanh\frac{4\pi}{2}\ldots}\,.\,\coth\pi\,.\,\coth 2\pi\,.\,\coth 3\pi\ldots,$$

it is brought into connexion with (δ) and (ϵ) (§ 23); and its value is thus found to be

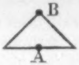
$$P_2=\frac{2\sqrt{2}}{\pi}\sqrt{\frac{\pi}{2K_0}}\sqrt{\frac{\pi}{2^{\frac{3}{4}}K_0}}=\frac{2^{\frac{5}{8}}}{K_0}.$$

Hence $$Q^5=\frac{2^{\frac{5}{2}}}{K_0^5},\text{ or }Q=\frac{\sqrt{2}}{K_0}.$$

In other words, the resistance of a square plate with the poles arranged as in fig. 11 is given by (21), if for $m+n$ we read its value $\frac{5}{2}$, and consider α equal to $\frac{1}{2}$.

One more distinct case may be mentioned, namely the right-angled triangle shown in fig. 12. This also requires two factors raised to different powers; and the result is the expression (21) with $\alpha=\frac{1}{6}$.

Fig. 12.



[To be continued.]

V. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

[Continued from p. 14.]

IV.

Separation of Ice, or of a Hydrate, or of the Anhydrous Salt, from solutions of Salts below 0° C.

§ 123. Very many determinations have been made of the solubility of various salts in water at temperatures ranging from 0° C. to the temperature of ebullition of the saturated salt solution. To Gay-Lussac, to Kremers, to Regnault, and others are due several series of exact determinations in this direction of research. But the examination of the phenomena of solidification which take place in salts of certain strengths at temperatures below 0° C. has suffered comparative, almost complete, neglect. And this appears to have arisen partly from the circumstance that it has been asserted by some philosophers, and denied by others entitled to equal respect, that when a solution of a salt below 0° C. begins to solidify by loss of heat, the solid formed is pure ice. It has been my privilege to reconcile the opposing views by the discovery of the fact which I trust now to have fully established, that when a salt solution which is already any fraction of a degree below 0° C. is cooled, one of three things must happen; and which of them happens is determined with the same salt by the strength of the solution.

1. In all solutions weaker than the cryohydrate, ice is formed, at temperatures which are lower according as the solution is richer in salt.

2. In solutions of a certain strength (namely that of the cryohydrate), combination of the salt and water take place in definite ratio and at a constant temperature. The solution is therefore a melted cryohydrate, and solidifies as a whole.

3. When solutions stronger than the cryohydrate, below 0° C., are cooled, either the anhydrous salt or some hydrate richer in salt than the cryohydrate separates.

It follows that the cryohydrate may, and indeed must inevitably be reached both by cooling a solution weaker than the cryohydrate (ice separates, the solution strengthens, the temperature sinks), and by cooling a solution stronger than the cryohydrate (anhydrous salt or a hydrate richer than the cryohydrate separates, the solution weakens, the temperature sinks). Assuming as a fact that which will be abundantly proved, namely that every salt which is soluble above 0° C. is also soluble below 0° C. (we shall see that there is even no quantitative discontinuity at 0° C. in the solubility), it follows immediately that a solution of any degree of strength whatever gives rise on cooling, sooner or later, to a liquid which remains unsolidified until the proper ratio and temperature is reached, and then solidifies in that constant ratio and at that constant temperature. From a solution of the strength of the cryohydrate nothing separates until the proper temperature is reached. And then, however rapid the absorption of heat may be, the temperature never sinks lower until solidification is complete.

§ 124. I propose in the present communication (1) to trace the history of solutions weaker than the cryohydrates as they yield ice on cooling, and (2) to examine the separation of anhydrous salts or hydrates richer than the cryohydrates when solutions richer than the cryohydrate are cooled. With regard to the first of these branches of inquiry, the only experiments in this direction which I have described are those relating to chloride of sodium in § 10, and those concerning spirits of wine in § 96.

A solution of a salt below 0° C. which is stronger than the cryohydrate, may be viewed as a solution in the cryohydrate, either of a hydrate richer than the cryohydrate or of the anhydrous salt. A solution of a salt below 0° C. which is weaker than the cryohydrate may be properly regarded as a solution of ice in the cryohydrate. A solution of chloride of sodium stronger than its cryohydrate may be also regarded as a solution of the subcryohydrate, $NaCl\,2\,H_2O$ (?), in the cryohydrate (§ 15).

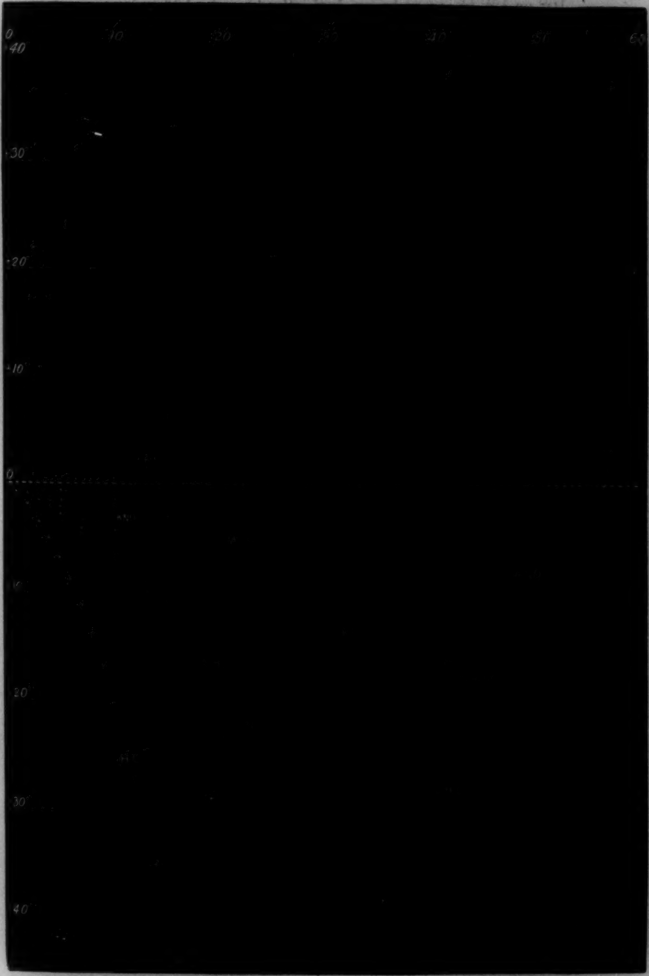
Just as a given weight of water dissolves at temperatures above 0° C., with rare exceptions, more of a salt the higher the temperature, so a given weight of the cryohydrate dissolves more ice at higher temperatures, below 0° C., than at lower ones. The weaker a given weight of a salt solution below 0° C. is, the smaller is the weight of the cryohydrate in it, and accordingly the less is the weight of ice which the given weight of solution is capable of dissolving. Experimentally, this appears in the results of all my experiments to be described below, that the stronger a solution of any given salt is (being weaker than the cryohydrate), the lower is the temperature below 0° C. to which it must be brought in order to yield ice; and the stronger a solution of any given salt is (being stronger than the cryohydrate), the less need its temperature be depressed in order to yield the anhydrous salt, or a hydrate richer in salt than the cryohydrate. And, as before stated, the latter kind of separation is quite continuous with the separation of such bodies at temperatures above 0°, such as is exhibited in the ordinary Tables of solubilities referred to in § 123.

§ 125. Almost all the numerical results are represented graphically in fig. 1. The abscissæ are in all cases the percentages of the anhydrous salt in the water. The ordinates, − or +, are the temperatures Centigrade below or above 0° C. at which solid matter begins to separate on cooling the solution. The point of reflexure (that is, the lowest point of each tracing) shows the temperature at which the particular cryohydrate is formed, and also the percentage of anhydrous salt in the cryohydrate. The left-hand branches of the tracings exhibit the temperature at which ice separates from solutions of the respective salts of the corresponding percentage composition. The right-hand branch of each tracing shows the temperatures at which the anhydrous salt or a hydrate richer than the cryohydrate is separated. The parts of these branches above the zero-line show the ordinary solubility of the same salts above 0°. The figure is reduced from my drawing, in which the percentages and tenths were centimetres and millimetres; and the degrees C. and their tenths were also centimetres and millimetres. The actual observations, being dotted off, were joined by straight lines.

§ 126. *General remarks on the experiments.*—Whenever possible, the solutions of the salts examined were made by dissolving weighed quantities of the anhydrous pure salt in quantities of water measured from a Mohr's burette. The grammes and centimetres were those of the percentages; that is, to form a 20-per-cent. solution, 20 grms. of the salt and 80 cubic centims. of distilled water were employed. Now and then a control mixture formed by weighing only was examined; but it appeared that the sources of error introduced by measuring instead of weighing the water were vanishingly small compared with the unavoidable errors of observation, notably those mentioned in the next paragraph.

Supersaturation.—With every salt solution from which we wish to get solidification by means of cooling, we have to guard against supersaturation. The notion that in order to start the crystallization of a supersaturated solution crystals must be present in the air identical in chemical kind with those ready to be formed in the solution, seems to be disproved by the fact that supersaturation in regard to ice is of the very commonest occurrence. In many cases a salt solution which should yield ice at a temperature $-t^\circ$ refuses to do so until $-(t^\circ + 5^\circ \text{ or } 6^\circ)$ is reached; then ice-crystals are formed through the mass and the temperature rises. Although we may indeed imagine ice-crystals to be floating in the air about the surface of the cryogen, we can scarcely conceive these microscopic crystals to

Fig. 1.



travel unmelted through the surrounding air, which may be at 10° or 15° C., so as to reach the liquid. And if it be argued that the origin of the ice-crystals may be at or near the surface of the salt solution in the experimental tube, I reply that crystallization from a supersaturated solution occurs both when it is covered with a layer of oil and when only the lower part of such a solution is acted on by the cryogen.

Method of observation.—Since the separation of ice strengthens the solution, it is necessary to determine the temperature of the very beginning of the ice-formation. The salt solution is cooled in a test-tube until some ice is formed; this is very nearly completely remelted under constant stirring with the thermometer, and then the tube is plunged momentarily into the cryogen. The minute spicula of ice so formed are again nearly remelted. The mean of four or five readings of the thermometer when the minute quantity of ice begins to increase is taken as the true temperature of ice-formation. In order to save time and start the crystallization of ice in a solution which one has reason to suppose is supersaturated with ice, the thermometer-bulb may be plunged into the cryogen and rapidly wiped dry, or into the mercury-cup to be described immediately. It soon becomes clothed with a film of ice-crystals from the moisture of the air. These are indeed almost invisible, and far too small in quantity to alter the strength of the salt solution when brought into contact with it, but amply sufficient to determine the separation of ice if the solution be supersaturated in regard to that body.

When the tube containing the salt solution is plunged into the cryogen till crystallization begins and then removed, portions of the cryogen adhering to the tube may carry the ice-formation too far, and by soiling obscure the tube. It is therefore found convenient to have standing in the freezing-mixture a short wide-mouthed bottle of mercury, and for the final observations to plunge the tube into this and so avoid soiling.

The solutions stronger than the cryohydrate were treated in a similar manner.

For the solubilities of the various salts at 0° I kept the solutions, previously saturated at 12° C., for three hours at 0°, and determined the strengths by evaporation &c., in some cases by determination of one constituent by the usual chemical means. I find these latter determinations agree very closely with those of Kremers throughout. Indeed, as will be seen, we seldom differ more than 0·3 per cent. For the determination of the temperatures above 0° C. at which salts and their hydrates separate, I have found, contrary to my anticipations, the more exact method to be in most cases to warm a given weight of the salt with its proper percentage of water in a stoppered bottle till solution was effected, and then by repeated observation find the temperature of incipient crystallization, rather than attempt to keep the water and salt for a length of time at a constant temperature and then determine the strength. The latter method, however, is of course especially available for 0° and 100° C.

§ 127. *Separation of Ice, of Subcryohydrate and of* NaCl *from solutions of that salt.*—The following Table (XVI.) shows the temperature below 0° C. at which ice begins to be separated from solutions of common salt of different strengths. In selecting these strengths I have chosen several close to the critical points, namely to that of distilled water, to that of the cryohydrate, and to that of saturation. And in the case of other salts I have, as far as possible, examined solutions of the same percentage-weight strengths. The ascent (see fig. 1. NaCl) is so steep from the cryohydrate to 0° C. that I have only been able to introduce one observation. As my determination for 0° C. was 26·27 (§ 11), and Poggiale's was 26·28, I have no hesitation in adopting Poggiale's for + 25° and + 40°.

TABLE XVI.

NaCl per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which a solid is formed.	Nature of solid.
1	99	− 0°·3	Ice.
2	98	− 0·9	„
3	97	− 1·5	„
4	96	− 2·2	„
7	93	− 4·2	„
10	90	− 6·6	„
13	87	− 9·1	„
15	85	−11·0	„
16	84	−11·9	„
19	81	−15·5	„
20	80	−17·0	„
22	78	−20·0	„
23·6	76·4	−22·0	Cryohydrate.
25	75	−12·0	Subcryohydrate.
26·27	73·73	0·0	NaCl.
26·5	73·5	+25·0	„ (Poggiale).
26·8	73·2	+40·0	„ (Poggiale).

This Table is to be regarded as replacing Table VI. in § 10 as far as the two are comparable. I bracket the subcryohydrate and the NaCl together, because the range of ratio is so small for a great temperature-difference that I cannot at present undertake to say within two or three degrees the temperature-range peculiar to each body.

§ 128. *Separation of Ice or Anhydrous Chloride of Ammonium from solutions of that salt.*—The following Table (XVII.) shows the temperature of solidification of solutions of NH_4Cl of various strengths.

TABLE XVII.

NH_4Cl per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid.
1	99	−0°·4	Ice.
3	97	− 1·6	"
5	95	− 3·1	"
7	93	− 4·6	"
10	90	− 7·1	"
13	87	− 9·9	"
15	85	−12·0	"
16	84	−13·0	"
17	83	−14·0	"
18	82	−15·0	"
19	81	−15 8	"
19·27	80 73	−16·0	Cryohydrate.
20	80	−15	NH_4Cl.
22	78	− 5	"
23·2	76·8	0	"
25	75	+ 8	"
30	70	+32	"

It will be seen that I make now the solidifying-point of the cryohydrate −16 instead of −15. This agrees with its temperature as a cryogen. The tracing of NH_4Cl in fig. 1 is seen to pass through the 0° line without deflection. Like the NaCl line it has a point of contrariflexure, but not so near the cryohydrate as with the latter salt. The determination at 0° C. was derived from the analysis, 12·1852 of the liquid gave 2·7721 of NH_4Cl.

§ 129. *Separation of Ice or Anhydrous Nitrate of Potassium from solutions of that salt.*—Nitrate of potassium being far less soluble below 0° C. than the two preceding salts, and its cryohydrate not differing much from the saturated solution at 0°, I have not attempted to get any temperature-values between the two; but I have carefully followed the form of the tracing up to the cryohydrate, and also above 0°.

TABLE XVIII.

KNO_3 per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid.
1	99	$-\overset{\circ}{0}$·1	Ice.
2	98	−0·3	"
3	97	−0·7	"
4	96	−1·1	"
5	95	−1·5	"
7	93	−2·2	"
8·5	91·5	−2·6	"
10	90	−2·9	"
11·2	88·8	−3·0	Cryohydrate*.
12	88	0·0	KNO_3.
13	87	+2·0	"
15	85	+6·0	"
20	80	+14·0	"
25	75	+21·0	"
35	65	+35·0	"
40	60	+41·0	"

The composition at 0° C. was derived from the analysis by evaporation of 11·8050 grms., which gave 1·4166 of KNO_3, or 12 per cent. (Gay-Lussac found 11·68).

§ 130. *Separation of Ice and Hydrate of* $CaCl_2$ *from solutions of that salt.*—Although troublesome to manipulate, I preferred to make the solutions by weighing the anhydrous chloride

TABLE XIX.

$CaCl_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	$\overset{\circ}{0}$·2	Ice.
2	98	0·5	"
3	97	1·1	"
4	96	1·6	"
5	95	2·1	"
7	93	3·3	"
10	90	5·5	"
15	85	10·5	"
20	80	17·5	"
28	72	27·5	Cryohydrate.
36·45	73·5	37	Unknown hydrate.
39	61	0	$CaCl_2+6H_2O$.
45 (Gerlach)	55	15·5	"

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* I have adopted the temperature −3°, after a long series of experiments, instead of −2°·6, which is given in Table X.

The determination at 0° C. was made by estimating the chlorine as chloride of silver. There is such little difference between the composition of the cryohydrate and the hydrate separated at 0°, that I have been unable to estimate the composition at intermediate temperatures. There is no evidence of the formation of any other hydrate than the one usually regarded as containing six molecules of water. On account of the difficulty of exactly measuring such low temperatures as are here concerned at the maximum, I have less confidence in the exactness of the form of the tracing of this salt than of any other.

§ 131. *Separation of Ice from a solution of Hydrochloric Acid.*—Although I have made a separate study of the hydrogen salts of several of the acids, I may here adduce one instance, namely that of hydrochloric acid, in order especially to compare the forms of the temperature-curve of a body which is, as far as we know, without a cryohydrate [*], with the curve-forms of metallic salts, all of which have cryohydrates within the range of artificial cold.

By a silver determination I found that 3·2726 grms. of a pure acid contained 1 grm. of HCl and 2·7734 grms. of water. From this acids of unit percentage weights were formed.

Table XX.

HCl per cent. by weight.	H_2O per cent. by weight.	Greatest cold as cryogen.	Temperature at which solidification begins.	Nature of solid.
		°	°	
1	99	......	− 0·7	Ice.
2	98	......	− 2·0	"
3	97	−2·0	− 3·6	"
4	96	......	− 5·3	"
5	95	−2·6	− 7·0	"
6	94	......	− 9·0	"
7	93	−4·0	−11·5	"
8	92	......	−14·0	"
9	91	−4·6	−17·0	"
10	90	−4·9	−20·5	"
12	88	−6·2	−27·0	"
14	86	−7·6	−35·0	"
16	84	−8·0	−45·0	"

The tracing of these values is shown on fig. 1, and may be compared with that of spirit of wine derived from the numbers given in § 96, Table XI. In neither tracing is there any decided indication of contrariflexure, although the spirit-of-wine tracing passes through its cryohydrate. In the centre column of Table XX. is given the greatest cold when used as cryogens that these acids can produce. The acid was in all cases at 12° C. The great specific heat of the water in which the HCl is dissolved prevents, of course, the attainment of the degree of cold equal to that necessary to solidify a cryohydrate, as is the case with those true salts which do not heat on hydration.

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[*] A cryohydrate of HCl has recently been described by a French chemist.

§ 132. *Separation of Ice or Anhydrous Bromide of Potassium from solutions of that salt.*

TABLE XXI.

KBr per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 3°	Ice.
20	80	− 7·1	„
30	70	−12·0	„
32·15	67·9	−13·0	Cryohydrate.
33	67	− 9·8	KBr.
34	66	− 5·0	„
35·03	65	0	„
(Kr.) 39·7	60·3	+20	„
(Kr.) 43·2	56·8	+40	„

The solubility at 0° was found from an experiment in which 11·2939 grms. of solution gave 3·9566 grms. of KBr. As Kremers found 34·5, I have adapted his determinations at + 20° and + 40° by adding 0·5 to the numbers he gives.

§ 133. *Separation of Ice and Anhydrous Iodide of Potassium from solutions of that salt.*

TABLE XXII.

KI per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	− 2·2°	Ice.
20	80	− 5·1	„
30	70	− 9·0	„
40	60	−14·4	„
52·07	47·93	−22	Cryohydrate.
55·93	44·07	0	KI.
(Kr.) 58·9	41·1	+20	„
(Kr.) 61·4	38·6	+40	„

Having found that 10·3681 grms. of the solution saturated at 0° C. contained 5·7990 of KI, or 55·93 per cent., and since Kremers found 55·86, I have adapted his determination for the 20° and 40° temperatures by adding 0·1 per cent. to his results. The ascent of the tracing (fig. 1) between the cryohydrate and 0° is too abrupt for the insertion of any intermediate value which shall be trustworthy.

§ 134. *Separation of Ice and Anhydrous Sulphate of Ammonium from solutions of that salt.*—The salt was dried at about 100° C., finely powdered, kept at 100° C. for ten hours, and kept for three days and nights in an exhausted receiver over sulphuric acid.

TABLE XXIII.

$(NH_4)_2SO_4$ per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	−2·6°	Ice.
20	80	−6·0	"
28·6	71·4	−10·8	"
40	60	−16·0	"
41·7	58·3	−17·0	Cryohydrate.
41·9	58·1	0·0	$(NH_4)_2SO_4$.
(H.S.) 43·2	56·8	+19·0	"

I have for the temperature 19° adopted H. Schiff's determination. Of all the salts which I have examined, the sulphate of ammonium shows in its tracing the greatest precipitousness in its ascent from the cryohydrate to the 0° C. ratio. It is in this region undoubtedly very nearly a straight line. The solubility at 0° C. was found from the data, 13·2512 of the solution gave 5·5522 of the salt obtained anhydrous by the means mentioned above.

§ 135. *Separation of Ice or Nitrate of Ammonium from solutions of that salt.*—The nitrate of ammonium used was dried at 100° C., finely crushed, and heated to incipient fusion; it ceased to lose weight but showed no trace of the nitrite. In the determination of the solubility at 0° C. it was treated in the same manner.

Table XXIV.

NH_4NO_3 per cent. by weight.	H_2O per cent. by weight.	Temperature Centigrade at which solidification begins.	Nature of solid formed.
10	90	$-\overset{\circ}{3}{\cdot}5$	Ice.
20	80	$-7{\cdot}0$	,,
30	70	$-11{\cdot}5$	,,
40	60	$-17{\cdot}0$	,,
43·7	56·3	$-17{\cdot}2$	Cryohydrate.
47	53	$-12{\cdot}0$	NH_4NO_3.
51	49	$-5{\cdot}7$	,,
54·1	45·9	$0{\cdot}0$	,,
(Kar.) 66·5	43·5	$+18{\cdot}1$	,,

The solubility at 18°·1 is the observation of Karsten. The shape of the tracing of this salt bears a remarkable resemblance to that of nitrate of potassium (see fig. 1). The gradual slope of its right-hand branch enabled me to insert two determinations there. Also noteworthy is the comparison between the tracing of this salt and that of the sulphate of the same base. Running together with near coincidence down to their cryohydrates, which are nearly identical in temperature and not far apart in percentage of salt, the one rises more abruptly than any other curve; the other is, with one exception, the most gradual.

§ 136. *Separation of Ice and Hydrated Sulphate of Magnesium from the solutions of that salt.*—The analysis of crystallized sulphate of magnesium in regard to its water by direct estimation is rather unsafe, on account of the high temperature required to drive off the last traces of water, and the decomposition of the salt at a somewhat higher temperature. I therefore determined the sulphuric acid in a sample of the sulphate I was about to use, and found that it was nearly the so-called hepthydrate. The determination of the solubility at 0° C. was also derived from a sulphuric-acid determination. Taking every 1·96 grm. of the crystallized salt as containing 1 grm. of $MgSO_4$, the following solutions were examined:–

TABLE XXV.

$MgSO_4$ per cent. by weight.	H_2O per cent. by weight.	Temperature T at which solidification begins.	Nature of solid formed.
5	95	− 0°·6	Ice.
10	90	− 1·5	„
15	85	− 3·0	„
20	80	− 4·8	„
21·86	78·14	− 5·0	Cryohydrate.
21·9	78·1	0·0	$MgSO_4 + 7H_2O$.
25	75	+15·0	„
30	70	+31·0	„

As my determination of the solubility at 0° C. (21·9) differs considerably from some of those given by others (Gay-Lussac 20·5, Graham-Otto 20·5, Pfaff 21·9), I determined for myself the solubilities above 0°.

§ 137. *Separation of Ice or Cryohydrate or Anhydrous Nitrate of Silver from a solution of that salt.*—I have not yet described the temperature and composition of the cryohydrate of this salt. A solution saturated at 0° C. and further cooled gives rise to an abundant crop of iridescent scales, which on examination prove to be the anhydrous nitrate. This continues till −6°·5, when the opaque cryohydrate is formed. The solution, however, is particularly prone to double supersaturation. A solution may sometimes be cooled to −8°; and during this, while the crystals of the nitrate fall, ice-crystals are formed which float. By and by the true cryohydrate is formed on the side of the glass; and then both separate crystallizations cease. This double supersaturation is entirely prevented by introducing a fragment of the previously formed cryohydrate into the mother-liquor which is being further cooled. The temperature remains then constant at −6°·6 to the last drop. The final crop being remelted gave, on analysis, the following results:—14·3538 grms. gave 6·9442 grms. of $AgNO_3$, or 48·38 per cent. of $AgNO_3$ in the cryohydrate. The cryohydrate has accordingly the composition $AgNO_3 + 10{\cdot}09\ H_2O$. The temperature −6°·5 is obtained on employing nitrate of silver as a cryogen. There are few more beautiful colourless bodies than the cryohydrate of silver. Opaque, lustrous, and semimetallic, it is somewhat heavier than the liquid in which it is formed.

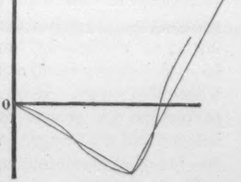
Of a solution saturated at 0° I found that 6·3581 grms. gave 3·5068 of the anhydrous nitrate, or 55·01 per cent. Kremers found 54·9; and accordingly I have availed myself of his determinations for the solubilities above 0° C. by adding 0·1 to his percentages.

TABLE XXVI.

$AgNO_3$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
10	90	$-\overset{\circ}{0}{\cdot}8$	Ice.
20	80	$-2{\cdot}7$	"
30	70	$-4{\cdot}7$	"
40	60	$-6{\cdot}0$	"
48·3	51·7	$-6{\cdot}5$	Cryohydrate.
50	50	$-5{\cdot}5$	$AgNO_3$.
53	47	$-2{\cdot}2$	"
55	45	$0{\cdot}0$	"
(Kr.) 69·4	30·4	$+19{\cdot}5$	"

§ 138. *Thoughts suggested by* fig. 1.—As the whole field of inquiry contained below the zero-line of fig. 1 has, I believe, remained hitherto unexplored, I am tempted to submit a few remarks upon it. First, of course, the tracings should be continuous curves between 0° and the cryohydrates, and again between the latter and the boiling-point of the saturated solutions, and doubtless, under pressure, beyond. Further, it seems that the curves are all varieties of the same kind. The figure 2 shows what we may liken to the backbone of the curve, with a typical curve about it. There is no absolute measure of what may be called the eccentricity of the curve, because there is no common measure between percentage composition and temperature; both are measured in arbitrary units. But this does not affect the type or order of the curve's equation. On the left-hand branches there appears to be a point of contrariflexure. The only apparent exceptions to this are KI, alcohol, and HCl. Concerning the two lat-

Fig. 2.



ter, doubtless we only see a fragment of their curves before their final cryohydrates. If there be such a point with KI it must lie between 40 per cent. and the cryohydrate, which is well possible. There seems to be a point of contrariflexure also on the right-hand branch, though sometimes the curvature is so small that this point is practically obliterated. The average slope of descent to the cryohydrate is invariably less than the slope of ascent thence to zero. Indeed every tangent to the left-hand branch of each curve makes a more acute angle with the zero axis than any tangent to the right-hand branch of the same curve. If this be true throughout, the unknown right-hand branch of the HCl curve must be very nearly at right angles to the axis of 0° C. There is no evidence to show that the right-hand branch is continuous with the left-hand. In the case of the halogen salts this almost appears to be distinctly shown not to be the case. If the branches be continuous, it appears that the colder the cryohydrate the less the curvature there. If the branches be discontinuous, the colder the cryohydrate the more acute is the angle between the tangents at the intersection of the curves. This rule holds good in all cases; but between NaCl and KI there is considerable difference of sharpness at the cryohydrate, attending identity of temperature. It is not the case that the deeper the valley the more precipitous the ascent, travelling from left to right; nor is it true that the deepest valley has the widest mouth. That is, salts the most soluble at 0° do not have the coldest cryohydrates, and therefore do not form the most powerful cryogens.

In the shape of the bottoms of the valleys (that is, the curvature about the cryohydrates) the curves of the oxygen salts show a likeness to one another as distinguished from the halogen salts. Considering the former by themselves, we might be inclined to view their two branches as being in all cases continuous. To settle the question decisively whether these curves are continuous, hundredths of degrees would have to be read with precision, and the initial formation of ice noted within that range. If we judge by the aspect of the halogen curves and the general continuity in properties between the halogen and the oxygen salts, I am inclined to consider the two branches discontinuous in all cases.

The tracings assume, of course, somewhat different positions if they are referred to molecular ratio instead of to absolute-weight ratio. Without determining each tracing for all its intermediate values, we may join by straight lines the points representing the molecular solubility at 0° with the molecular value of the cryohydrate. While each of these lines is, of course, parallel to the corresponding line derived from fig. 1, being got by determining its extremities by division of the percentage by the molecular weight, such division necessarily brings those lines relatively further towards the left whose salts have heavy molecules. The extreme points of the lines are got by dividing the percentage values of fig. 1 by the molecular weights and multiplying by 100. I know no property of the salts here under examination which would have enabled us to predict the position and inclination of these lines. Neither are the water-worths of the salts as cryohydrates nor their solubilities in water at 0° C. in any obvious accord with their known properties.

Correlation between the Boiling and the Glaciation of Salt Solutions.

§ 139. Looking upon the phenomenon of solution as being brought about by the exercise of the force, physical affinity, and regarding the act itself as being in the first instance caused by the prevalence of what may be called physical adhesion (as distinguished from mechanical) between the water and the salt over the sum of the physical cohesions of the water and of the salt, we must after the first contact (that is, when some of the salt is dissolved) regard the contest as between the physical adhesion between the salt and the solution of it on the one hand, and on the other the physical cohesion of the salt together with the physical cohesion of the solution of it. By an increase of temperature the physical cohesion of the salt is lessened. By the solution of more salt the physical adhesion between the salt and the solution is lessened. Thus a partially saturated solution so far resembles what some chemists call a partially saturated atom, that it exhibits not necessarily a lesser energy, but always a lesser capacity for saturation than a still less saturated one. (Witness anhydrous sulphate of magnesium compared with the crystalline salt.) Let us suppose that at a temperature t° a weight w of water dissolves $\frac{1}{n}$ of s, the weight of the salt. Then using the symbol $\frown$ to denote either physical adhesion or cohesion, we have the condition of equilibrium or saturation expressed by the equation

$$s\left(1-\frac{1}{n}\right)\frown\left(w+\frac{s}{n}\right)=s\left(1-\frac{1}{n}\right)\frown s\left(1-\frac{1}{n}\right)$$
$$+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right).$$

Or, since the tensions of physical adhesion and cohesion are independent of quantity,

$$s\frown\left(w+\frac{s}{n}\right)=s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right).$$

At a temperature $t_{,}^{\circ}$,

$$s\frown\left(w+\frac{s}{n+d}\right)=s\frown s+\left(w+\frac{s}{n+d}\right)\frown\left(w+\frac{s}{n+d}\right),$$

where d is $+$ or $-$ according generally as $t_{,}^{\circ}$ is $>$ or $<$ than t°.

The expression

$$s\frown\left(w+\frac{s}{n}\right)>s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right)$$

implies that the water is not saturated ; while

$$s\frown\left(w+\frac{s}{n}\right)<s\frown s+\left(w+\frac{s}{n}\right)\frown\left(w+\frac{s}{n}\right)$$

implies that it is supersaturated. The above equations are the general ones for all salt solutions above 0° C. For temperatures below 0° C. another element manifests itself with greater force as the temperature is lowered, namely the physical affinity between the solid salt and solid water. If in fig. 1 we draw a straight line parallel to and below the zero axis so as to cut any one tracing in two points (it never can be cut in more than two points), we see that solidification may ensue at the same temperature in two differently strong aqueous solutions of the same salt. The intersection with the left-hand branch is the condition of equilibrium resulting from the equality between:—on the one hand, ice $\frown$ ice together with salt $\frown$ water ; on the other, salt solution $\frown$ water,

$$\text{ice} \frown \text{ice} + s \frown w = \left(w + \frac{s}{n}\right) \frown w.$$

The intersection on the right-hand branch shows the conditions under which there is equilibrium between:—on the one hand, salt $\frown$ salt (or hydrate of salt $\frown$ hydrate of salt) together with the salt solution $\frown$ salt solution; on the other, salt solution $\frown$ salt or hydrate,

$$\text{salt} \frown \text{salt} + \left(w + \frac{s}{n}\right) \frown \left(w + \frac{s}{n}\right) = \left(w + \frac{s}{n}\right) \frown s.$$

Looking upon the cryohydrate as a common value, we have

$$\text{ice} \frown \text{ice} + s \frown s + \text{ice} \frown s = \left(\frac{s}{n} + \frac{w}{m}\right) \frown w + \left(\frac{s}{n} + \frac{w}{m}\right) \frown s.$$

§ 140. Compare now the decomposition of a salt solution by the loss of heat with the decomposition by gain of heat when such a solution boils. And in instituting this comparison, we must bear in mind how much more sensitive to variation in pressure is the boiling- than the solidifying-point.

(1) A solution poorer than the cryohydrate loses heat; ice is formed.	(1) A solution poorer than that saturated at a given temperature receives heat; vapour is formed.
(2) This goes on until the proportion of the cryohydrate is reached, the temperature falling.	(2) This goes on until saturation is reached, the temperature rising.
(3) The cryohydrate may be reached by freezing out ice from a weaker solution, or by any other withdrawal of water.	(3) Saturation may be reached by evaporation, boiling, or any other withdrawal of water.
(4) When ice separates from a liquid, it remains in contact with the liquid, and endeavours to redissolve therein.	(4) Vapour separated from a liquid is removed from the field of contention, unless the liquid be enclosed with the vapour.
(5) When by the separation of ice the proportion of the cryohydrate is reached (nearly independent of pressure), ice and the salt separate simultaneously.	(5) When by the separation of vapour the proportion of saturation is reached (very dependent upon pressure), vapour and the salt separate simultaneously.
(6) The two bodies (ice and the salt) being crystallizable	(6) One being a solid and the other a vapour, they do not

solids, unite to form a crystallizable cryohydrate which exhibits a constant gravimetric composition.	unite, but in their separation preserve a constant gravimetric ratio under like conditions of pressure.
(7) A cryohydrate in the act of solidification shows identity of composition between the solid and liquid portions. The temperature of solidification is constant.	(7) A saturated solution, when boiling, shows the same ratio between the vapour formed and the salt precipitated as exists between the liquid water present and the salt it holds in solution. The temperature of boiling is (under like pressure) constant.

§ 141. A cryohydrate undergoing solidification may therefore be considered physically as the homologue of a saturated salt solution in the act of boiling. For absolute comparison we should have to eliminate pressure, or rather make automatic pressure the measure of the effect of elimination. Wüllner (Pogg. *Ann.* Bd. cx.) found that the vapour-tension of a salt solution varied inversely with the amount of salt it contained. Thus at 51°·8 the vapour-tension of aqueous solutions of chloride of sodium, in mercury pressure, were found to be:—

H_2O.	NaCl.	millim.
100	0	100
90	10	94
80	20	88

Wüllner also found that the diminution of the vapour-tension effected by a given percentage of the salt increases as the vapour-tension increases; that is, the diminution is greater as the temperature is greater. Looking upon vapour-tension as the mechanical equivalent of effort at separation, we find that it has its perfect counterpart in the left-hand branches of the curves of fig. 1. Compare the quantity of vapour with the quantity of ice. The left-hand branches are nearly straight lines; but they are on the whole clearly concave downwards. The variation in the nature of the salt also affects the vapour-tensions; and on constructing the curves of vapour-tension of different salts in solutions of different strengths, we see that the ice-curve is algebraically continuous with the vapour-tension curve. The same may be also seen if we assume that the atmospheric pressure, being constant, will not affect the order of curvature of the curves representing the ratio of salt in a solution and its boiling-point.

§ 142. The fact that the separate constituents of a solution of the proportion of a cryohydrate are both of one form of matter, of course favours their combination. With boiling aqueous solutions the dissimilarity of the educts is generally unfavourable to their union. There is ample evidence, however, of a similar, though less definite (because more influenced by pressure), reunion of the constituents of certain solutions. If an indefinite quantity of dilute alcohol be rectified 100 times at a constant pressure in such a manner that the first (say half) portion is redistilled, the water is never eliminated, nor does the strengthening extend beyond a definite limit. Perhaps the experiments bearing most directly upon this train of thought are those of Roscoe and Dittmar on the hydration of acids. Since, for instance, nitric acid containing 80 per cent. of HNO_3 is weakened on boiling (considering the residual body), and an acid containing 60 per cent. is strengthened by boiling, until in both cases an acid containing nearly 70 per cent. of HNO_3 is got, which boils at 120° C. at 760 millims., this body was viewed as a definite hydrate. Roscoe showed that this acid, if it be boiled at a lower or higher pressure, is itself decomposed. So with hydrobromic, hydrochloric, and hydriodic acids, with sulphuric acid, and with ammonia. We have here physical ratios conditioned by pressure. Without doubt the cryohydrates would vary in composition if they were formed at enormous pressures; for the variation effected by pressure in the freezing-point of water is not likely to be precisely the same as the variation in the solidifying of a salt out of a solution. Trifling as these differences would assuredly be under all conditions of variation of artificial pressure, the thought is not remote that we may have to refer the extraordinary variation in quantity of the elements of some perfectly well crystallized and constantly composed minerals from what is sometimes called the atomic ratio to the enormous pressure attending their genesis. The fact that such composition may be represented on paper by the complex manipulation of ratios known amongst laboratory products, can only be admitted into the argument when their formation can be shown in the laboratory by means such as may be fairly supposed to exist in nature. In a word, under vast changes of temperature and pressure, the gravimetric saturating quantities, or "atomic weights," of elementary substances may vary. And it is perhaps noteworthy that this conception, which has urged itself upon us with rare force in the consideration of the relations by weight of bodies in union at extremely low temperatures, is the same as that which has been brought forward by some of those who have examined the relation of the elements when subjected to the high temperature and abnormal pressure of the sun's mass, which has, as a doctrine of continuity, commended itself to some of the most philosophic chemists, and which is certainly in harmony with the conception of dynamic energy, whether of mass or mere velocity.

Our chemistry, as it is generally understood, is the chemistry of one atmosphere pressure.

Separation of Ice from Solutions of Mixtures of Salts.

§ 143. In III. §§ 109–122, I proved that on cooling a saturated solution of two salts, the temperature of the cryohydrate, when reached after separation of various quantities of the constituents, was never sensibly lower than that of the constituent which had the lowest of the two cryohydrate temperatures. In these experiments I was careful to use the salts in such proportion that recombination in integral quantity was possible. In the series of experiments now to be described, where ice has to be separated from a mixture while the salts themselves remain in solution, we may, in those cases at all events where no double decomposition is possible, take equal weights of the salts, so as to compare the results with those of fig. 1; and for this study I will here confine myself principally to the two nitrates $AgNO_3$ and NH_4NO_3, because nitrates are especially free from tendency to form double salts, and because the tracings of the ice-separating temperatures of the individual salts are of widely different range and character.

§ 144. *Separation of Ice from mixed Solutions of the Nitrates of Silver and Ammonium.*—The following are all 20 per cent. solid.

Sol. 1.	$AgNO_3$ . .	20 grms.	gave ice at $-\overset{\circ}{4}{\cdot}3$.
	NH_4NO_3 . .	10 ,,	
	H_2O . . .	120 ,,	
Sol. 2.	$AgNO_3$ . .	20 ,,	,, ,, $-5{\cdot}0$.
	NH_4NO_3 . .	20 ,,	
	H_2O . . .	160 ,,	
Sol. 3.	$AgNO_3$ . .	20 ,,	,, ,, $-5{\cdot}5$.
	NH_4NO_3 . .	30 ,,	
	H_2O . . .	200 ,,	
Sol. 4.	$AgNO_3$ . .	10 ,,	,, ,, $-5{\cdot}8$.
	NH_4NO_3 . .	20 ,,	
	H_2O . . .	120 ,,	

The following are all 30 per cent. solid :—

Sol. 5.	$AgNO_3$ . .	30 grms.	gave ice at $-6{\cdot}8$.
	NH_4NO_3 . .	15 ,,	
	H_2O . . .	105 ,,	
Sol. 6.	$AgNO_3$ . .	30 ,,	,, ,, $-8{\cdot}0$.
	NH_4NO_3 . .	30 ,,	
	H_2O . . .	140 ,,	
Sol. 7.	$AgNO_3$ . .	20 ,,	,, ,, $-8{\cdot}9$.
	NH_4NO_3 . .	30 ,,	
	H_2O . . .	116·6 ,,	
Sol. 8.	$AgNO_3$ . .	20 ,,	,, ,, $-9{\cdot}1$.
	NH_4NO_3 . .	40 ,,	
	H_2O . . .	140 ,,	

On comparing these results with those given in fig. 1 (showing the ice-tracings for the separate salts, which are also 20 and 30 per cent. solid), the following results are obtained in regard to the comparative influences of nitrate of silver and nitrate of ammonium in retaining ice in solution.

TABLE XXVII.

Solution.		Calculated.	Found.
20 per cent.	1. $AgNO_3 = 2\ NH_4NO_3$	$-\overset{\circ}{4}\cdot 1$ C.	$-\overset{\circ}{4}\cdot 3$ C.
	2. " $= 1$ "	$-4\cdot 8$	$-5\cdot 0$
	3. " $= \frac{2}{3}$ "	$-5\cdot 3$	$-5\cdot 5$
	4. " $= \frac{1}{2}$ "	$-5\cdot 5$	$-5\cdot 8$
30 per cent.	5. " $= 2$ "	$-6\cdot 9$	$-6\cdot 8$
	6. " $= 1$ "	$-8\cdot 1$	$-8\cdot 0$
	7. " $= \frac{2}{3}$ "	$-8\cdot 8$	$-8\cdot 9$
	8. " $= \frac{1}{2}$ "	$-9\cdot 2$	$-9\cdot 1$

The calculated numbers are got under the hypothesis that the influences of the constituents of the mixture are proportional to their masses. That is, if there be n grms. of A and m grms. of B, each being a p per cent. solution, and if A alone gives out ice at t_1 and B at t_2, then (t being the temperature at which the mixture gives up ice)

$$t = t_1 + \frac{n}{n+m}(t_2 - t_1);$$

and the numbers found do not differ from those calculated more than may be attributed to errors of observation.

§ 145. *Separation of Ice from the mixed Sulphate and Nitrate of Ammonium.*—Of the 10-per-cent. solution of the sulphate of ammonium 20 grms. were taken; of the 10-per-cent. solution of the nitrate of ammonium 10 grms. were taken. The mixture of these gave up ice at $-3^{\circ}{\cdot}2$, which is exactly the temperature calculated from the above equation, the glaciating points of the two solutions being $-2^{\circ}{\cdot}6$ and $-3^{\circ}{\cdot}5$ respectively. We may assume therefore, generally, that the temperature of glaciation of a mixture of two salt solutions of the same percentage strength is a mean between the glaciation-temperatures of its constituents, when new salts are not formed. This chapter, however, will require a great amount of further work, especially for those cases where the constituent solutions of the mixture are not of the same strength.

§ 146. *Further examination of Iodide of Sodium.*—In conclusion I am very glad to be able to throw a clear light on the anomalous and exceptional behaviour of the iodide of sodium. From §§ 65, 68, 69, it appears that while as a cryogen this salt gives the temperature $-26^\circ\cdot5$, it solidifies as a cryohydrate at -15°. A large quantity of the iodide, purified by several recrystallizations, was dissolved to saturation at 12° C., and very gradually cooled to 0°. The crystals given up in this range proved to be anhydrous iodide. On further cooling to -12°, a second crop of crystals was formed, which also proved anhydrous. Between -12° and -20° but little further solidification occurred. When -23° was reached rapid solidification began, and the temperature rose to -15°. In another similar case the temperature sank to -24° before solidification began. The whole becomes of a dough-like pastiness. The crystals are long, silky needles; they remain transparent. On further cooling in a chloride-of-calcium cryogen to -26°, the silvery opacity due to a true cryohydrate is produced, and the whole becomes of a stony hardness. It is clear, therefore, that with the iodide as with the chloride of sodium there are two cryohydrates:—the subcryohydrate, having a melting- and solidifying-point at -15°; and another, which in combination with the first has a melting- and solidifying-point at $-26^\circ\cdot5$. We have therefore to look for the true (that is, lowest-temperatured) cryohydrate in solutions weaker than that analyzed in § 65, which had 59·45 per cent. With the chloride of sodium there is no difficulty in separating the subcryohydrate; the latter body falls as iridescent scales, and leaves the residual liquid clear. With the iodide of sodium no such mechanical separation ensues, and no artificial separation demanding the maintenance of so low a temperature would be trustworthy.

To get at the composition of the true cryohydrate it must be approached from the other side—not from saturated, but from dilute solutions (see § 123). I have accordingly examined in succession the temperatures at which ice or other body separates from *percentage* solutions of NaI.

TABLE XXVIII.

NaI per cent., by weight.	H_2O per cent., by weight.	Temperature C. at which solidification begins.	Nature of solid separated.
5	95	− 0·7	Ice.
10	90	− 2·1	„
15	85	− 3·9	„
20	80	− 6·0	„
25	75	− 8·5	„
30	70	−11·8	„
35	65	−15·2	„
40	60	−20·5	„
45	55	−26·0	„
49·2	50·8	−30·0	Cryohydrate.
50	50	−29·5	Subcryohydrate.
55	45	−20·0	
60	40	−14·7	„
61·6	38·4	0·0	NaI.
63·6	36·4	+13	„

With regard to the first eight determinations there is nothing particular to remark. For the 40-per-cent. solution a $CaCl_2$ cryogen had to be used. Finding that ice separated from the 45 solution, and the subcryohydrate from the 50 solution, I concluded that the composition of the true cryohydrate must lie between these values. I accordingly submitted several ounces of the 45, and also of the 50 solution to a carbonic-acid cryogen. From the first ice separated; from the second the subcryohydrate. The temperature sank in both cases to −30°, and there remained constant, while from both crop after crop of the pearly-white true cryohydrate was formed. After about three quarters of each had been thus removed, the temperature still remaining at −30°, the residual liquids were analyzed by evaporation and strong heating.

Of 45 solution 10·9945 gave 5·3982 NaI or 49·1 per cent.
Of 60 „ 14·6176 „ 7·1932 „ „ 49·2 „

Accordingly the true cryohydrate is reached from either side. The water worth of this salt is 8·603. It would only be possible to deduce the composition of the subcryohydrate if we knew the relative quantities of the two present, as well as the composition of their compounds. The reason why the dry iodide does not give the temperature of −30° when used as a cryogen is no doubt because, like chloride of calcium, it evolves a large amount of heat in coming into contact with water. But in spite of this deficit, the temperature of the cryogen is governed, as we have seen it to be before, by that of its coldest constituent. The speculation concerning iodide of sodium in § 69[*] is fully justified.

For the solubility at 0°, a solution saturated at 8° was kept for three hours at 0° C. Of this, 10·7932 grms. contained 6·6486 grms. of this salt: this gives 61·6 per cent.; Kremers found 61·3.

§ 147. No salt can well be more favourable than the iodide of sodium for the study of double supersaturation. The values of the solution between 49·2 and 61·6 show this phenomenon in a remarkable manner. Thus a solution of 60 per cent. may be kept for hours at −20°. It may be stirred, shaken, particles of dust and particles of NaI may be thrown in, a glass rod covered with a film of hoar-frost inserted, it remains quite limpid. Cooled a few degrees lower, it becomes suddenly semisolid, and rises to −15° or −14° in temperature. At values approaching the cryohydrate, but rather less strong, it may happen, as the excess of water is removed by cold, that instead of the cryohydrate being formed when the right strength is reached, the subcryohydrate is produced continuously with the further separation of ice. The one set of crystals floats, the other sinks. This occasional state of things is the most perfect counterpart of the simultaneous separation of water as vapour and the salt when a saturated solution boils, considered in § 140. A drop or two of the same solution, suddenly cooled to opaque solidification, determines the formation of the true cryohydrate.

I beg the reader to note the following corrections of, and additions to, Table X. § 88. In the case of correction, the corrected number is marked with *, the previously given number being placed in brackets.

Formula of salt.	Temperature of cryogen.	Temperature of solidification of cryohydrate.	Water-worth.	Per cent. of salt.
Add ...... $CaCl_2+3H_2O$	−33	−37	11·8	36·45
Correct... NaI	−26·5	−30*(−15)	8·6	49·2
Correct... NH_4Cl	−16	−16*(−15)	12·4	19·27
Add ...... $AgNO_3$	− 6·5	− 6·5	10·09	48·38
Correct... KNO_3	− 3	− 3*(−2·6)	44·6	11·20

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[*] In this paragraph read "cryohydrate of iodide of sodium" instead of "cryohydrate of sodium."

VI. *Remarkable Atmospheric Phenomena in Ceylon. By the* Rev. R. Abbay, *M.A.*[*]

One of the most startling and extraordinary of all atmospheric phenomena may be seen during fine weather from the summit of Adam's Peak in Ceylon. This mountain rises extremely abruptly from the low country, and by its elevation of 7200 feet above the sea commands a most extensive and map-like view of all the low lands to the south-west and north-west for a distance of 50 miles or more up to the sea coast. The upper part of the mountain is an acute cone of solid rock, some 2000 feet or more in height, that rises in perfect isolation above the range of which it forms a part, and also above all the neighbouring mountains to the east and north. The phenomenon, which is described by all who have witnessed it as of the most striking character, is seen at sunrise, and consists *apparently* of an enormous elongated shadow of the mountain projected to the westward, not only over the land but over the sea, to a distance of 70 or 80 miles. As the sun rises higher it rapidly approaches the mountain, and appears at the same time to rise before the spectator in the form of a gigantic pyramid of shadow. Distant objects, a hill or a river (or even Colombo itself, at a distance of 45 miles), may be distinctly seen through it, lighted up by the sunlight, diffused most probably by the surrounding illuminated atmosphere; so that the shadow is not really a shadow on the land, but a veil of darkness suspended between the observer and the low country. All this time it is rapidly rising and approaching, and each instant becoming more distinct, until suddenly it seems to fall back on the spectator, like a ladder that has been reared beyond the vertical; and the next instant it is gone. Of the accuracy of the above facts I have no doubt whatever. A great number of trustworthy witnesses have described it to me; and but for a sudden attack of fever at the foot of the peak, which prevented an ascent being made in the evening, I should have been able to describe it from personal observation. As it was I ascended next day and was able to form a very good idea of the conditions under which the phenomenon takes place; but I was, of course, unable to obtain accurate data as to the duration of the veil, the height to which its apex rises above the horizontal, the elevation of the sun, &c. If I am right in supposing that no explanation has ever been offered of this remarkable appearance, the following remarks, which appear to be fairly satisfactory, may perhaps not be uninteresting. The average temperature at night in the low country, during the dry season when Europeans ascend the mountain, is between 70° and 80° F., whilst that on the summit of the peak is from 30° to 40° F. Consequently the lower strata of air are much less dense than the upper; and an almost horizontal ray of light passing over the summit, must of necessity be refracted upwards and suffer total internal reflection as in the case of an ordinary mirage. This may be readily seen by a reference to fig. 1, where a nearly horizontal ray passing over the summit of the peak P suffers total internal reflection at A, and is deviated upwards in the direction A B; or when a less horizontal ray is refracted at C, reflected at D, and refracted again at E, it finally issues along the line E F. It will be evident from fig. 1 that the shaded parts represent the veil of darkness at three different moments of time, and also that the veil appears to rise as its base approaches the mountain, *i. e.* as the sun rises and the rays fall less horizontally.

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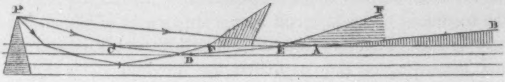
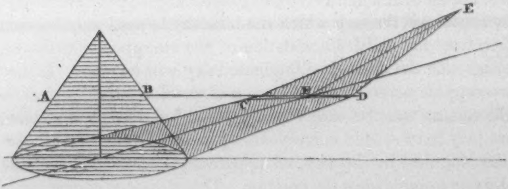
[*] Read May 27, 1876.

Fig. 1.



By referring to fig. 2 it will be seen how the aerial shadow

Fig. 2.



of the upper part of the peak, *i. e.* the part above A B, suffers total internal reflection, and is thrown upwards into the air as C E D. It will also be evident, by comparing the two figures, that as the veil of darkness approaches it must tend to assume a more vertical position until it reaches the critical angle when total internal reflection ceases and the veil suddenly disappears. Its apparent tilting over on the spectator I imagine to be merely an illusion produced by the rapid approach and rising of the dark veil without any gradual disappearance which can be watched and estimated. It will be evident that it is the illumination of the innumerable particles floating in the atmosphere, and capable of reflecting light, that causes this aerial shadow to be visible by contrast.

Another atmospheric phenomenon visible in Ceylon, of great interest but not so striking in character as the above, admits of an equally simple explanation. Not unfrequently in the mountain districts broad beams apparently of bluish light may be seen extending from the zenith downwards, converging and narrowing as they approach the horizon. This ray-like appearance is very similar to that seen before sunrise; only the point from which the rays proceed is *opposite* the sun: the rays themselves are very broad and blue in colour; and the spaces between them have the ordinary illumination of the rest of the sky. If we suppose in this instance that the lower strata of air are colder than the upper (a condition of the atmosphere which not unfrequently occurs in a tropical mountain district like that of Ceylon, where large currents of heated air sweeping up a valley cross another valley nearly at right angles and at a considerable elevation above it), the refraction spoken of in the case of Adam's Peak will be downwards instead of upwards. If, too, the observer be *below*, the veil of darkness will appear to him like a very elongated triangle apex downwards, or broad ray, through which the blue sky beyond may be seen free from the palish illumination of the atmosphere, whilst on either side the ordinary illuminated sky will be seen. If now we suppose several isolated masses of cloud to partially obscure the sun, as was the case when I witnessed the phenomenon, we may have several corresponding inverted veils of darkness, like blue rays in the sky, all apparently converging towards the same point below the horizon. This apparent convergence of the beams is merely an effect of distance, as in the case of parallel rays of light from the rising or setting sun, the blue rays being practically parallel bands in the atmosphere devoid of illumination. It will be evident that conical-shaped clouds are not necessary to produce this effect. Isolated clouds of any massive form would be sufficient to throw the bands of shadow through the illuminated atmosphere, and refraction and perspective would do the rest. The above phenomenon is called by the Singhalese "Buddha's rays;" and though according to Sir Emerson Tennent it is very varied in character and appears in different parts of the sky, yet I have only seen it when the sun was low at evening and when the rays converged to a point, apparently directly opposite the sun; and I do not think it possible for the phenomenon to be seen in any other position.

VII. *Model of a small Electrical Machine.*

By GEORGE FULLER, *C.E., Belfast*[*].

THIS machine is a double-acting electrophorus worked by cranks, with the addition of an arrangement by which a small electric charge given to it is augmented and kept up, so that the dielectric does not require to be recharged.

A is a vulcanite plate supported in a vertical position by two insulated standards, *p*, *p*.

B, B′ are two insulated metallic plates, one on each side of the plate A; these can be moved together to and from contact with A by means of cranks worked by the handle C.

m and *n* are two conductors armed with needles and connected by means of two glass rods, so that they receive the same reciprocal motion from the mechanism by means of the wire, cord, and pulleys, *g*, *g*, *g*. The wire *g* is attached to the arm that moves the plate B′; and the length of the cord and size of pulley are so adjusted that when this is in its extreme position from A, as shown, *m* and *n* are also at one extremity of their motion, as shown; and when B and B′ are in contact with A, *m* and *n* are horizontal. The conductor *n* is not insulated; and it will be seen by the diagram that *m* and *n* during their motion pass on either side of the plate A.

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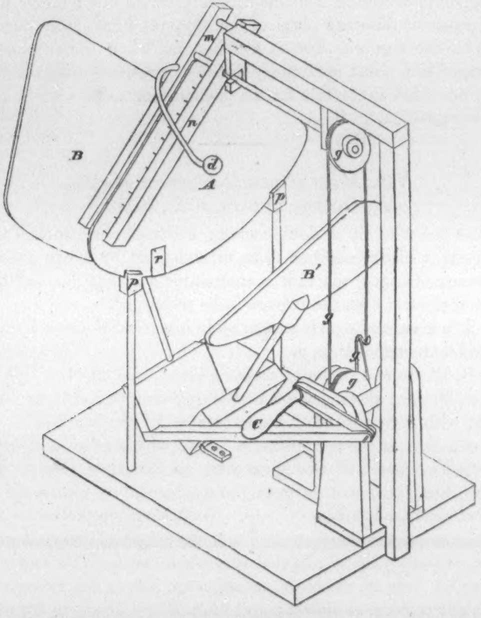
[*] Read June 24, 1876.

To the conductor *m* is fixed a wire terminating in a brass ball, *d*; this wire is of such length and form that when B and B′ recede from A, and *m* and *n* move downwards from their horizontal position, the ball *d* passes close to B′. Care has to be taken that this juxtaposition does not occur until the vulcanite plate separates the points on *m* and *n*.

The action of the instrument is as follows:—A charge of, say, negative electricity having been given to the insulated arm *m* when in a vertical position, on motion being given to the machine this electricity is distributed by means of the points over the face of the vulcanite next to B; at the same time positive electricity is drawn from the earth, thrown upon the other face of that plate by the uninsulated points attached



to *n*. When now B and B′ are brought into contact with A, the negative electricity on its one face attracts the positive on the conductor B and repels the negative, whilst the positive on its opposite face attracts the negative on the conductor B′ and repels the positive; then, by means of the piece of tinfoil (*r*) that connects B and B′ when they are in contact with A, the two electricities that are repelled neutralize each other; and when the plates are moved away from the vulcanite, B is charged with positive and B′ with negative electricity. Then, before reaching its extreme position, the latter communicates its charge to the insulated arm *m* by the brass ball *d*, and its negative electricity is thus distributed over the surface of A next to B and thus augments its original charge. At the end of its path B′ is momentarily connected to earth. It will be evident that on again bringing the plates into contact the charge in B is augmented; also that if a supply of negative electricity is required, the only modification of the above is to give to *m* a charge of positive instead of negative electricity.

The above instrument forms an easily constructed and worked electrical machine, and is beside interesting as rendering automatic the classical electrophorus of Volta.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

June 24, 1876.

VIII. *On Salt Solutions and Attached Water.*

By Frederick Guthrie.

[Continued from p. 79.]

V.

(1) *Separation of Ice, Salt, Hydrate or Cryohydrate from Salt Solutions* (continued).

§ 148. *Separation of Ice &c. from Solutions of Chloride of Barium.*

Table XXIX.

$BaCl_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	$-\overset{\circ}{0}\cdot9$	Ice.
10	90	$-2\cdot2$	„
15	85	$-4\cdot0$	„
20	80	$-6\cdot0$	„
21·83	78·17	$-7\cdot5$	Cryohydrate.
23·98	76·02	$0\cdot0$	$BaCl_2+H_2O$.
30	70	$+25$	„

I again found the temperature of the cryogen to be $-7^{\circ}\cdot3$ ($-7^{\circ}\cdot2$, § 78), and the temperature of the cryohydrate to be $-7^{\circ}\cdot5$ to -8°. But it is seen that as derived from a dilute solution I now find the cryohydrate to contain only 21·83 per cent. of $BaCl_2$, while in § 78, where it was derived from a saturated solution, I found 23·2. No doubt the smaller of these numbers is the more correct. The composition of the cryohydrate was derived from the following data. 6·5151 of melted cryohydrate gave 1·5225. The water-worth is accordingly 41·357. The solubility at 0° C. was derived from the following:—

	1.	2.	Mean.
Solution . .	6·7830	7·9470	
$BaCl_2$ . . .	1·6214	1·9119	
Per cent. . .	23·90	24·06	23·98

§ 149. *Separation of Ice &c. from Solutions of Protosulphate of Iron.*

TABLE XXX.

$FeSO_4$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	−0°·2	Ice.
10	90	−0·8	"
14·5	85·5	−2·0	Cryohydrate.
14·9	85·1	0·0	$FeSO_4+7H_2O$.

As in § 148, I find the composition of the cryohydrate to show somewhat less salt than previously (§ 82), where the cryohydrate was obtained from a saturated solution, and where the amount of salt was determined by simple evaporation. I now find the melting-point of the cryohydrate to be −2° C.; and the temperature of the cryogen is exactly the same. In the above-given determinations of the cryohydrate and of the solubility at 0° C. the solution was oxidized with nitric acid, the sesquioxide was precipitated with ammonia and weighed; the amount of $FeSO_4$ was thence deduced. For the cryohydrate,

4·8076 grms. gave 0·3676 Fe_2O_3, or 0·6984 $FeSO_4$.

The water-worth is therefore 49·8. For the solubility at 0° C.,

7·7890 grms. gave 0·6080 Fe_2O_3, or 1·1552 $FeSO_4$.

§ 150. *Separation of Ice &c. from Solutions of Tribasic Phosphate of Sodium and Hydrogen*, $Na_2HPO_4+2H_2O$.—This, the most usual phosphate of sodium, when used as a cryogen only reduces the temperature to −1°·0 C. The cryohydrate also melts at the same temperature (I found −0°·9).

Owing to this short range of temperature it is impossible to examine the separation of ice from solutions of various strengths. The determinations were made by reducing the salt to a bibasic pyrophosphate of sodium. For the cryohydrate,

	1.	2.	Mean per cent.
Solution .	6·5760	9·3401	1·72 of $Na_4P_2O_7$, or
$Na_4P_2O_7$.	0·1119	0·1627	1·83 of Na_2HPO_4.

The water-worth is accordingly 852.

The following gave the solubility at 0° C. :—

6·7277 grms. of solution gave 0·1264 of $Na_4P_2O_7$, or 2·0 per cent. of Na_2HPO_4.

§ 151. *Separation of Ice &c. from Solutions of Nitrate of Sodium.*

TABLE XXXI.

$NaNO_3$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	− 2°	Ice.
10	90	− 4·2	„
15	85	− 6·3	„
20	80	− 8·4	„
25	75	−10·8	„
30	70	−13	„
35	65	−15·5	„
40·80	59·2	−17·5	Cryohydrate.
42·34	57·66	0	$NaNO_3$ or subcryohydrate.

There appears to be a subcryohydrate of a composition intermediate between 40·80 and 42·34 per cent. For the determination of the composition of the cryohydrate I refer to § 75. The solubility at 0° C. was derived from the data; 6·0660 of solution gave 2·5682 of $NaNO_3$. It is remarkable that Marx found 44·4 per cent. and Poggiale 44·3 per cent. of the anhydrous salt. The salt I employed was made from the pure bicarbonate, and was entirely free from sulphates and chlorides. As in all similar determinations, I was not content to surround the flask containing the nitrate with ice; for I never find that by this means the temperature in the flask sinks to 0° C. A few grains of salt are added to the ice; and the temperature, as indicated by a continually agitated thermometer in the solution, remains for four or five hours at 0° C.

§ 152. *Separation of Ice &c. from Solutions of Nitrate of Lead.*

TABLE XXXII.

$Pb\,2(NO_3)$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	−0°·3	Ice.
10	90	−0·5	"
15	85	−0·7	"
20	80	−1·2	"
26·23	73·77	−2·5	Cryohydrate.
29·89	70·11	0·0	$Pb\,2(NO_3)$.

The temperature of the cryogen is −2°·5. The solutions were analyzed by simple evaporation and gentle heating.

§ 153. *Separation of Ice &c. from Solutions of Nitrate of Barium.*—As the solution of this salt was found to contain only 5·37 per cent. of the anhydrous salt at 0° C., and as the cryohydrate only contains 5·3 (§ 80), only one intermediate observation on the separation of ice could be got, namely that of the 3-per-cent. solution, which gave up ice at −0°·4.

§ 154. *Separation of Ice &c. from Solutions of Nitrate of Strontium.*

TABLE XXXIII.

$Sn\,2(NO_3)$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	−0°·5	Ice.
10	90	−1·2	"
15	85	−2·3	"
20	80	−3·8	"
26	74	−6	Cryohydrate.
29·62	70·38	0·0	$Sn\,2(NO_3)$.

§ 155. *Separation of Ice &c. from Solutions of Nitrate of Calcium.*

TABLE XXXIV.

$Ca\,2(NO_3)$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	− 1°·1	Ice.
10	90	− 2·3	"
15	85	− 4·2	"
20	80	− 6·5	"
25	75	− 9·3	"
30	70	−12·9	"

I have not yet got the cryohydrate of nitrate of calcium. As a cryogen it gives a temperature of −16°.

§ 156. *Separation of Ice &c. from Solutions of Acetate of Sodium.*

TABLE XXXV.

$NaC_2H_3O_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	− 2·2°	Ice.
10	90	− 5·1	”
15	85	− 9·1	”
20	80	−14·0	”
22	78	−16·0	”
23·3	76·7	−18·0	Cryohydrate.
26·6	73·4	0·0	$NaC_2H_3O_2 + ?H_2O$.

The temperature of the cryogen is exactly −18°. For the cryohydrate determination, 7·7032 grms. gave 1·7963 grm. of $NaC_2H_3O_2$. For the solubility at 0°, 4·7473 grms. gave 1·2646 of $NaC_2H_3O_2$. The water-worth is 30. The solid constituent was estimated by simple evaporation and heating to incipient fusion.

§ 157. *Separation of Ice &c. from Solutions of Acetate of Potassium.*

TABLE XXXVI.

$KC_2H_3O_2$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
5	95	− 2°	Ice.
10	90	− 4·6	”
15	85	− 7·4	”
20	80	−11·2	”
25	75	−16	”
30	70	−22·5	”

The solubility at 0° C. was measured both by directly weighing the dried and fused acetate, and by converting it into a nitrate by frequent treatment with nitric acid and evaporation,

1. Direct.	2. Indirect.
6·8131 solution gave	7·4837 solution gave
4·2083 $KC_2H_3O_2$, or	4·8573 KNO_3, or
61·8 per cent.	62·8 per cent. $KC_2H_3O_2$.

Mean . . . . 62·3.

The cryohydrate of acetate of potassium has not yet been determined.

The temperature of the cryogen of acetate of potassium is −25° C.

It is well known that fused acetate of potassium is heavier than the anhydrous solid acetate at the same temperature ; but I do not find the remarkable fact anywhere noticed, that the fused anhydrous salt is also lighter than the aqueous solution of the salt saturated at ordinary temperatures (17° C.).

(2) *A few Organic Crystalloids in Aqueous Solution; their behaviour on being cooled and on being heated, and as Cryogens.*

§ 158. *Cane-sugar.*—Sugar-candy was finely powdered and dried at 100° C. in a current of dry air.

Table XXXVII.

$C_{12}H_{22}O_{11}$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
5	95	$-\overset{\circ}{0}$·3	Ice.
10	90	−0·5	„
15	85	−0·9	„
20	80	−1·3	„
25	75	−1·8	„
30	70	−2·4	„
35	65	−3·2	„
40	60	−4·1	„
45	55	−5·4	„
50	50	−7·0	„
51·4	48·6	−8·5	Cryohydrate.
(Mean) 67·33	32·67	0·0	$C_{12}H_{22}O_{11}$.

Solutions stronger than the cryohydrate may be cooled below -8°·5 before solidification begins. A 60-per-cent. solution does not show signs of solidification above -11°·4. The solid which separates, however, is sugar. This is a consequence of the supersaturability of sugar solutions, and the possibility of the condition of supersaturation being maintained even in solutions from which crystals of sugar are being deposited. Also, as was so notably the case with alcohol, the cryohydrate is an abundant solvent for sugar. The cryohydrate of saccharose was analyzed by evaporation.

2·2658 grms. gave 1·5244 grm. of saccharose, or 51·4.

For the solubility at 0° a solution saturated at +20° was kept for three days and nights at 0° C.

$$\left.\begin{array}{r}3\cdot6300\\4\cdot1175\end{array}\right\}\text{ gave }\begin{array}{l}2\cdot4510\\2\cdot7640\end{array}\text{ of saccharose or cane-sugar.}$$

Since it will be shown in § 161 *et seq.* that the colloid forms of matter not only do not unite with water, but also do not depress the freezing-point of that liquid, it did not seem unlikely that on cooling below 0° a solution of raw sugar containing about 50 per cent. of solid matter, the solid cryohydrate would be formed and the sugar be freed from colloid impurities. As caramel certainly, and probably other foreign colouring-matters in raw sugar are colloids, I have succeeded in greatly purifying raw sugar by this method of cryohydration. Into the details of this I shall not here enter.

§ 159. *Glycerine.*—With regard to this substance a very remarkable circumstance may be noticed. That it is crystalloid we have had until lately (1) the indirect evidence depending upon its being an alcohol, and upon several alcohols being known in the solid and crystalline state, while others which are not so known yet unite with crystalline salts; (2) the direct evidence obtained from its diffusion through colloid septa. Lately it has been observed to assume the form of a crystalline solid. Again, it has lately been employed in aqueous solution in Pictet's ice-machine as a non-freezable liquid to yield heat to vaporizing sulphurous acid, and take it from water for the purpose of freezing the latter. The latter faculty of its solution to resist solidification below 0° C. proves, first, that it will form a cryogen, and, secondly, that it will form a cryohydrate—the latter fact again proving, as we shall see in § 161 *et seq.*, that it is a crystalloid.

Pure glycerine dried by being kept for a week over oil of vitriol *in vacuo*, when mixed with finely crushed ice forms a cryogen whose temperature is −19° C.

Table XXXVIII.

$C_3H_8O_3$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which solidification begins.	Nature of solid formed.
5	95	− 0°·8	Ice.
10	90	− 2·0	"
15	85	− 3·3	"
20	80	− 5·0	"
25	75	− 6·2	"
30	70	− 8·8	"
35	65	−11·5	"
40	50	−13·9	"
45	55	−16·7	"

I have not yet succeeded in obtaining the cryohydrate of glycerine.

As a cryogen the glycerine behaves as hydrochloric acid and other liquid elements of cryogens; namely, the temperature obtained is lower if the liquid be previously cooled.

§ 160. *Tartaric Acid.*—As a cryogen, tartaric acid gives the temperature −13°·5. I cannot say that I have cleared up all the ambiguities in the behaviour of this body. The separation of ice took place with regularity as far as the following solutions are concerned.

$C_4H_6O_6$ per cent. by weight.	H_2O per cent. by weight.	Temperature at which ice separates.
5	95	− 0°·7
10	90	− 1·4
15	85	− 2·5
20	80	− 3·7
25	75	− 4·7
30	70	− 6·3
35	65	− 7·6
40	60	−10·1
45	55	−13

Apparently continuous with these results is the separation of a solid at −16°·5 from a 50-per-cent. and of a solid at −17°·6 from a 55-per-cent. solution. But there is here really a breach of continuity. The 55-per-cent. gives up tartaric acid at −17° when crystals of that body are introduced. And it is difficult to say whether ice, or acid, or a cryohydrate is separated from the 50-per-cent. at −16°·5. If a 50-per-cent.

solution be cooled to −19° and a smaller portion of the same solution which has been solidified by an ether-carbonic-acid cryogen be introduced into the first, the temperature rises to −8°, and opaque crystals are formed, while that temperature is constantly maintained. The same body at the same temperature is formed even when the first solution has only been cooled to −14°. I think, therefore, that there is with tartaric acid a body similar to that which we encountered with the iodide of sodium, namely a subcryohydrate. Owing to the sirupy nature of these strong solutions at these low temperatures, and the very slow rate at which the separation of their constituents ensues, I do not think that analyses of such intermediate subcryohydrates would be sufficiently trustworthy for reproduction. But the cryohydrate which separates at −8° is distinct enough.

4·0735 grms. of solution gave 1·8972 grm. of $C_4 H_6 O_6$, or 46·6 per cent.

A solution kept for two days and nights at 0° showed the following composition: 5·1304 grms. of solution gave 2·7233 grms. of $C_4 H_6 O_4$, or 53·0 per cent.

(3) *Colloids in aqueous solution; their behaviour on being cooled and on being heated.*

§ 161. *Generalities.*—It is perhaps only by an extension of the definition that we can regard solutions of colloids as solutions of salts. It will be of great interest to examine how far the two classes of bodies resemble, and how far they differ from one another in aqueous solution. The substantial researches of Graham on the division of matter into crystalloids and colloids, resulting as they did in the discovery of a whole series of new and profoundly interesting bodies, threw a flood of light on molecular physics. He showed that colloid septa were permeable only to crystalloid liquids, and thus established among the molecular mechanism of matter a series of connected facts similar to and of no less importance than those which have of late attracted so much attention in the domain of radiation; for that sonorous undulations are absorbed by sympathetic vibrators, that radiation is arrested by the possible authors of such radiation, cannot long be separated from the fact that colloids arrest colloids by contact-continuity, while they are permeable (transparent, diathermanous) to crystalloids.

Recalling a few of the distinguishing properties of colloids, we find that when miscible at all with water they are miscible in all proportions. Accordingly one colloid cannot precipitate another from solution. Towards water they then behave as two gases behave towards one another. Some gelatinize (gelatine); others do not (gum-arabic). Some coagulate by heat (albumen) in association with water. In the dry state they are amorphous and show conchoidal fracture. I look upon a water-jelly as consisting of an indefinitely minute cellulation of a solid colloid enclosing liquid water. In a liquid water-colloid the solid colloid particles are present, but they do not form closed cells, and therefore do not with their contents resist change of form; nor are they necessarily in contact with one another. The viscosity of such a mass is due to friction between its solid and liquid parts. The elasticity of a jelly is due to the elasticity of its cell-walls. Thus I can form a model of a jelly by pressing together little caoutchouc bladders containing water: and in soap-suds I recognize a jelly of a higher order; that is, instead of solid we have liquid cell-walls, and instead of liquid we have gaseous contents. On heating or stirring the suds the bubbles burst, the liquid walls collapse and contract, not again to be formed automatically. On heating or stirring a jelly the solid colloid walls are broken, the liquid contents of the individual cells become continuous, so that all hydrostatic laws hold good. Let the heated liquid cool, and similar cells are restored; but on repeated heating, the cells are burst in such divers places that they are not to be restored. Such restoration is also hindered and prevented on stirring during cooling.

I gladly leave these speculations for the facts which gave them birth. Through the kindness of Mr. W. C. Roberts, F.R.S., there were placed at my disposal certain of the inorganic colloids prepared by the late Mr. T. Graham, the Master of the Mint. Some of these are spontaneously undergoing so interesting a change that I have been unwilling to disturb them. Others, notably a solution of silicic acid and of sesquioxide of iron in water, I find contain each under 1 per cent. of oxide. I prepared, therefore, fresh solutions, following the directions given by Mr. Graham, and meanwhile examined certain organic colloids.

§ 162. *Gum arabic.*—If a 1-, 5-, 10-, 20-, 25- or 30-per-cent. aqueous solution of gum arabic be cooled, ice begins to be formed in all cases at 0° C. exactly. Even a 35-per-cent. solution, which is very viscid, begins to give up ice at 0°, and is quite solid at $-0^{\circ}\cdot5$. A 45-per-cent. solution, which is semisolid, shows a temperature of -1° at the beginning of sensible ice-formation, and is certainly solid at $-1^{\circ}\cdot2$. This very small degree below 0° C. in so viscid a substance is certainly not more than may be attributed to the overcooling of the ice already formed. I can find no trace of a cryohydrate; and that such does not exist is supported by the fact that, in spite of the great solubility of gum in water, when powdered gum and ice are mixed together the resulting temperature is 0° exactly. Gum arabic is therefore powerless as a cryogen. It is true that this might be attributed to the gum acting like a certain quantity of anhydrous chloride of calcium, which when mixed with ice may compensate, by the liberation of heat of combination, for the heat absorbed in the joint liquefaction. But that such balancing does not ensue is shown by the fact that a 45-per-cent. solution of gum also gives 0° C. with ice, while a solution, however weak, of chloride of calcium will absorb heat when liquefying ice by contact. The same is also proved by the observation that when gum is mixed with water the alteration in temperature, though certainly in the direction of heat-liberation, is very inconsiderable. In a preliminary experiment I found that powdered gum and water mixed in indefinite proportions gave a rise of $0^{\circ}\cdot75$ C. As the result of a number of more exact experiments, it appeared that the greatest heat was developed when four parts by weight of water were mixed with one of finely powdered gum arabic; a rise of $1^{\circ}\cdot1$ ensued, namely from $15^{\circ}\cdot7$ to $16^{\circ}\cdot8$. The first temperature was that of the water in the outer of two concentric beakers, the inner of which contained the gum. The beakers were thickly wrapped and covered with flannel, and had been in such contact for several hours. To the above numbers, however, I do not attach much quantitative value; for, owing to viscosity, solution takes place very slowly. The results, however, clearly show that the heat developed is far too small to counteract any great heat-absorption by solution, and that accordingly the latter does not exist. The heat liberated is indeed scarcely more than the heat of capillarity.

I believe that most of us would have been disposed to predict that in order to boil a solution of gum a temperature above 100° C. would be required. This was, I confess, my own persuasion until I was enlightened by the above experiments on the separation of water as ice from gum-solutions of all strengths. But being so enlightened I was able to predict that a solution of gum would boil at a temperature not above 100° C. A 20-per-cent. solution of gum arabic appeared to boil in a test-tube over the bare flame below 100° C. But as it is almost impossible to avoid a certain amount of decomposition under these circumstances, a tube holding a fresh quantity of the 20-per-cent. solution was placed in a wider tube containing a solution of chloride of sodium which boiled at 104° C. On heating the latter gradually the gum-solution could be made to boil before the brine began to do so. And if by rapid heating the latter were made to boil, the gum-solution boiled violently, and continued to do so after the brine had ceased. A thermometer in the gum-solution showed 100° C. Further, a 40-per-cent. solution of gum arabic when surrounded by boiling water boils at 98° C., or two degrees lower than the water.

§ 163. *Albumen.*—Dry albumen when mixed with ice can only depress the temperature 0°·25 C. Four parts by weight of water and one of albumen, both at 18°·2, gave, on mixture, a temperature of 19°·5. In another experiment the common temperature rose from 19° to 21°. In the above experiments commercial albumen was used. For more exact experiments white of egg was used, which analysis showed consisted of 13·37 per cent. of albumen (dried at 100° C.) and 86·63 of water. Such white of egg begins to separate ice at 0° C., and freezes into a solid mass at −0°·5. A solution diluted to 5 per cent. begins to give up ice at 0° C., and is solid at −0°·2 C. A 10-per-cent. solution separates ice at 0° C., and forms a solid mass at −0°·3 C. The boiling-points of albumenoid solutions, of course, could not be determined. And the addition of alkalies to prevent coagulation would naturally vitiate the results.

§ 164. *Gelatine.*—The gelatine used in the following experiments was such as is commonly used by confectioners. Solutions of this substance containing 5, 10, 15 and 20 per cent. may be rapidly cooled under constant stirring without gelatinization. Ice in all such cases begins to be formed at 0° C.; and the whole becomes solid at that temperature. Stronger solutions are so difficult to manipulate, on account of their gelatinization and consequent hardness, that the results with them are doubtful. As far as the experiments extend, however, they fail to show that the freezing-temperature is affected.

A 20-per-cent. solution heated (as in § 162) in a brine-bath boiled at 99°·9 C. A 45-per-cent. solution boiled at 97°·5; and a 50-per-cent. solution, which is as stiff as the strongest glue used by cabinet makers, boiled also at 97°·5. A very striking and conclusive experiment is, to surround the tube containing the 50-per-cent. solution with distilled water in another tube If the exterior water-tube be heated slowly, the glue in the inner tube boils before the water in the outer one. On continually stirring the frothy viscid mass, the true boiling-point is observed to be constant at 97°·5.

As an experiment the above is exceedingly instructive, and, I believe, novel; but, like so many novel and instructive phenomena, it is one of daily occurrence. The blistering and frothing of the strongest glue when heated by steam or water in the outer pot has certainly been observed hundreds of times in every carpenter's shop. Is it strange or is it natural that so familiar a fact should never have struck us as requiring explanation?

§ 165. *Mixtures of organic colloids.*—To round off the series of experiments with colloids homologous with those of crystalloids, I next examined a mixture of gum arabic and gelatine. A solution was made containing 20 per cent. of gelatine, 20 of gum arabic, and 60 of water. This began to freeze and froze completely at 0° C. It boiled at 97°·7 C.

(4) *General remarks on colloids.*

§ 166. The depression of the boiling-point of water by the solution in it of organic colloids has its analogies. Amongst the metals innumerable instances occur to us in which the melting-point of an alloy is not only lower than that of one constituent, not only lower than the mean of the two, but lower than that of either or any of the constituents—witness the "fusible metals." When metals are alike in chemical affinities, they have little affinity for one another. They mix mainly by diffusion. They dilute one another. If we mix sodium with sodium, we certainly dilute each sodium with the other; the adhesion which we supply is exactly equal to the cohesion which we replace; the resulting mass is identical with its constituents. But if we mix potassium and sodium together, by diffusion we diminish cohesion, and the adhesion introduced is less than sufficient to replace it; from two solids we get a liquid. The similarity of the metals prevents their having any notable relationship with one another. Equally to the purpose is the recollection of the alteration in boiling-point which follows the mixture of liquids which are chemically neutral to one another. Many a month has been wasted in the attempt to get propylic alcohol from fusel oil, owing to the fact that a mixture of amylic and butylic alcohols will commence to boil at a temperature below the boiling-point of butylic alcohol. Moist ether boils below dry ether; and even a liquid such as iodide of ethyl, which is almost insoluble in water and which dissolves but little of that body, has its initial boiling-point already lower than that of water. The work done by the heat in separating the particles of a body is already effected by the interpenetration of the associated body. Cohesion is diminished and a less heat-tension is required to complete the separation of the more volatile constituent as vapour.

From another aspect we may consider the neutral body to act as an infinite series of points, and recall the fact that, on evaporating saturated solutions of various salts over a steam-bath, bubbles are frequently formed beneath the salt-pellicle, owing perhaps to the multiplicity of points, at temperatures certainly below 100° C., while the clear solution of the same salt when saturated demands a temperature several degrees above 100° C. for ebullition. The rise in temperature shown on mixing a dry colloid with water is probably connected with the deficit below 100° C. of the temperature required to boil the resulting colloid solution.

Returning to the separation of ice from colloid solutions, we must conceive that when ice so separates that the solution becomes enriched in regard to the colloid body, the particles of ice in contact with the source of cold become overcooled (that is, fall below 0° C.) on account of the insufficient circulation and the imperfect thermal conductivity of ice and of the colloid solution. But when such over-cooled ice is stirred with the colloid solution a fresh portion of ice is formed if the latter is already at 0° C.; if above 0° C., then some of the ice melts: in either case the 0° C. is restored. Ultimately the solid particles of the anhydrous colloid must lie side by side with the ice particles, as they do when the two are mixed as powders, as in § 162. They are as independent of one another as are the particles of ether and chloroform when the two are mixed, or as are the particles of two gases which diffuse through one another without combination.

I reserve the results which I have obtained with inorganic colloids for a future communication.

The figure shows the same constants as were shown in the figure, Paper IV., but with the new salts.

IX. *On some Phenomena of Induced Electric Sparks.*

By S. P. Thompson, *B.A.*, *B.Sc.*

[With a Plate.]

1. The observations communicated in this paper are the result of an investigation into the phenomena discovered in November 1875, in Newark, N. J., by Messrs. T. A. Edison and C. Batchelor, and alleged to demonstrate the existence of a new form of energy. A detailed memoir of the phenomena has since appeared in the 'Quarterly Journal of Science'[*], by Dr. G. M. Beard, of New York, who accepts, with some hesitation, the hypothesis of a new force.

2. When a galvanic current passing through the coils of an electromagnet is rapidly interrupted, minute bright sparks can, at the moment of interruption, be drawn from the electromagnet-core by an earth-wire or by any conducting substance

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[*] "The newly-discovered Force," by George M. Beard, A.M., M.D., New York (Quarterly Journal of Science, No. L. April 1876).

held in the hand and presented to the core*. These sparks are best seen when the electromagnet-coils, interrupter, and battery-cells are completely insulated from the ground. The substitution of a bar of any metallic substance, or even carbon or wood coated with tinfoil, in place of the iron core of the electromagnet, does not prevent the production of the spark. With bars of zinc or cadmium, or, better still, of either of these metals amalgamated on the surface, the sparks are brighter.

The minuteness of the sparks makes observation of them a matter of some difficulty; between two points of graphite pencils in a dark box they are more readily seen. They are conducted by all metallic bodies, and by the body; and even pass into insulated conductors of large surface, apparently requiring no completion of the circuit. This circumstance, however, as well as the supposed inability of the sparks to produce any indications upon the galvanometers and electroscopes of ordinary use, may be explained by a further knowledge of their nature. It was this apparent lack of polarity in the nature of the discharge that led to the adoption of the hypothesis of a new form of energy; and the assumption seemed further to be borne out by an apparent absence of physiological effect.

Two forms of the apparatus at first employed to produce the sparks in question are given in figs. 1 & 2. In the first case, where the circuit was rapidly interrupted by an automatic vibrator, the sparks were drawn from the electromagnet-core or from the vibrating armature. In the second they were drawn from a bar of metal placed above, but not in contact with, an electromagnet in a circuit completed by a depressor key.

3. Careful repetition of the experiments failed to elicit evidence of polarity in the spark, or to procure response to

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* As an interrupter almost any form will answer; a Morse key is good for slow interruptions by hand; or an automatic vibrator, similar to the "break" of an induction-coil may be employed. Similar sparks have doubtless been often noticed by those who have used any form of apparatus involving rapid interruption of the current, and as often attributed to defective insulation. The writer of this paper observed the same thing some years ago in a trembler of particularly good construction, and in vain rewound the coils in hope of eliminating the supposed leak.

the ordinary electrical tests. And the wish to obtain further information upon the nature of this peculiar discharge by studying its effects in illuminating the rarefied gases of vacuum-tubes, rendered it necessary to seek a means of more plentiful production, and to abandon the methods of the original investigators already described; for the sparks so obtained had never exceeded the quarter of a millimetre in length, and were quite incapable of producing a luminous discharge through a small vacuum-tube.

The following experiments led to the method desired:—

A rod of soft iron 20 centims. in length was wrapped in folds of vulcanized sheet rubber to a thickness of 2 centims. Around the exterior of this 150 centims. of stoutly insulated copper wire were wound. One end of this wire was connected with one terminal of the secondary wire of a small induction-coil *, the other end was brought within 15 millims. of the other terminal. The intent of this arrangement was to pass, as in the previous experiments, an intermittent current around a metallic conductor. When the coil was set in action the secondary currents passed with rapid discharge across the interval of about 15 millims. between the end of the wire and the terminal; and it was then found that sparks of several millimetres length could be drawn from the iron rod within the folds of vulcanized rubber by an earth-wire, or by the finger, or by any conductor held in the hand. It was found impossible to convey any charge from the iron rod by a proof-plane to an electroscope; and on leading a wire to a sensitive long-coil galvanometer by Colladon no deflection was obtained, though the sparks were drawn from the wire beyond the galvanometer, through which the force thus manifesting itself must therefore have passed. Identical effects followed the substitution of bars of copper, cadmium, and zinc for the iron rod.

It was next ascertained that no perceptible difference of potential existed between the two ends of the metal rod, and none between the ends and the median portion. The spark

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* This coil, capable of throwing sparks of 50 millims. length with two cells of Grove's element, was employed in most of the succeeding experiments. Each piece of apparatus used, including the cells of the battery, was carefully insulated from the table.

could be drawn indifferently at either end, or at the middle, but not from two points at once; nor could it be led by an insulated wire from one point of the bar to another. Other metallic objects in the neighbourhood of the bar became similarly affected; and from them sparks could be drawn. These effects were augmented when the distance of 15 millims. over which the secondary current of the coil discharged itself as a spark was increased to 20 millims. They diminished when the distance was reduced to 5 millims., and ceased entirely when the interval was reduced to nothing, so that the secondary current of the coil passed along unbroken metallic connexions. The conclusion to which these results pointed was apparently that the effect was one of surface-charge. This surmise might be directly tested by increasing the size of the metallic core and the number of surrounding turns of wire.

4. The arrangement next to be described*, and shown in diagram at fig. 3, was therefore directly suggested by the preceding experiments. It remained practically unchanged in the subsequent investigation. A large Leyden jar was taken and its inner and outer surfaces joined by a metallic wire, constituting it simply a conductor of large surface. Around it were wrapped sheets of vulcanized rubber to a thickness of 25 millims. About this again were coiled about 30 metres of stoutly insulated copper wire†. As before, one end of this wire was led to the terminal T′ (fig. 3)—the other

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* It will be plain, from the subsequent details, that this arrangement plays the part of an accumulator or condenser, the interior surface of which is represented by the Leyden jar, the exterior being represented by the wire coiled outside. A Leyden jar is not essential; any cylindrical conductor is as good if of large surface; and a sheet of tinfoil laid upon the exterior of the insulating material is more effective than 50 metres of covered wire wound round it. The precise form of the accumulator is immaterial; but thorough insulation must be secured. The above arrangement is preferred because its parts are analogues of those of the experiments that suggested it. The knob of the jar is moreover convenient for drawing sparks from.

† To avoid confusion, in fig. 3 the condenser arrangement is given in diagram, D standing for the insulating folds of rubber, P for one condensing surface (the external wire coils), Q for the other condensing surface (the Leyden jar, which acts in this combination as if made of one piece of metal).

end, *w*, being placed near the terminal T, and so adjusted that the distance *w* T might be increased or diminished at will.

5. When the coil was set in action, sparks could be drawn by an earth-wire, C, from the knob of the accumulator, Q. When the discharging-distance of the coil *w* T was less than 5 millims., the sparks drawn from Q were minute, not exceeding 1 millim. in length, destitute of perceptible physiological action, producing no deflection when led through an ordinary needle-galvanometer, and, as before, were incapable of imparting any charge to a proof-plane.

When *w* was removed to a distance of 10 millims. from T the sparks at Q were larger and brighter; when the distance was increased to 20, 25, and 30 millims. successively, the sparks drawn at Q were much more vivid and exceeded 10 millims. in length. These sparks, though producing comparatively little effect in contracting the muscles of the arm, were excessively painful and penetrating to the nerves of the skin. Their light was brightest when they passed between poles of zinc, mercury, or carbon. Their brilliance was augmented and their length was increased to above 20 millims. when *w* was withdrawn so far from T that only a faint brush discharge passed across from *w* to T, a distance of about 50 millims.; and a still greater effect was produced when T was directly connected with earth. This modification virtually changed the arrangement to that indicated in fig. 4*.

6. When the spark obtained between Q and the earth-wire C exceeds 4 millims. in length, it is capable of illuminating a small vacuum-tube. The illumination differs, however, in a remarkable manner from that produced by the ordinary direct discharge of the induction-coil. Instead of the usual phenomena of a small brush of light at the positive pole, and a

* Since the communication of these experiments to the Physical Society, my attention has been called to an article in the Journal of the Franklin Institute for June 1871, by Prof. E. J. Houston, of Philadelphia, where, under the title of "A New Connexion for the Induction-coil," he describes a somewhat similar arrangement, in which an insulated conductor is employed in connexion with the coil. With this combination Prof. Houston observed some curious effects of induction in neighbouring bodies; but he seems to have thought them due to escape of electricity, and apparently had no suspicion of the real nature of the sparks so produced.

bright aureole or glow surrounding the negative pole, the illumination is symmetrical, alike at each pole, having both brush and glow at each, and is unaltered by reversing the primary circuit of the coil. An occasional flash, however, seemed to glow at one pole or at the other.

On making single contacts by holding the break-piece of the induction-coil in the fingers the effect was as follows:—at each make-of-contact no illumination; at each break-of-contact an illumination of the same symmetrical nature, affording no evidence of polarity of discharge in one direction more than in another.

7. To ascertain whether the discharge at the two poles was simultaneous or alternating, a rotating mirror was placed beside the vacuum-tube. The images were found to be, roughly speaking, alternate, the discharges being alternately from either pole. The irregularity of the alternation appeared to be dependent partly upon the distribution of the resistances in the circuit, partly upon the irregularities in the vibrations of the break. The occasional flashes of light at one pole or the other were explained by the occasional appearance in the mirror of two contiguous images having the same position, indicating the occurrence of two consecutive discharges in the same direction.

With rotating slits the same phenomenon of reciprocating discharge was observed, though less advantageously.

8. One terminal of a long-coil Thomson's reflecting galvanometer, by Elliott Bros., was put to earth, the other being connected with Q (fig. 3). When the distance *w* T was less than 5 millims. no deflection was produced upon the needle and mirror, a tremor being the only result. But when the distance *w* T was gradually increased, and the secondary discharge had consequently to accumulate upon its conductors to acquire sufficient density to overleap the resistance of the increased thickness of air between *w* and T, the tremulous motion of the galvanometer-needle became much more marked, the spot of light wandering about on either side the zero of the scale, never at rest, but showing no permanent deflection. When the distance *w* T was increased to nearly 50 millims. the brisk flow of sparks gave place to the brush discharge, varied only by the passage of an occasional spark. In this

case the wanderings of the spot of light on the scale were still more exaggerated, the needle apparently being turned little by little with an increasing deflection during some twenty or thirty vibrations of the contact-breaker of the coil, then receiving a sudden impetus in the opposite direction as the secondary spark discharged across the interval *w* T. This result was entirely confirmatory of the occasional flashes previously observed in the vacuum-tube, with which, on further examination, the more violent oscillations of the galvanometer-needle were found to be simultaneous. The experiment also accords with the previous observations of physicists with respect to the oscillations of the induced currents of the coil. It explains, too, why with an ordinary needle-galvanometer no deflection had been obtained with the minute sparks yielded by the earlier experiments.

9. Having again diminished the distance *w* T to 5 millims., a wire was led from Q to the knob of a gold-leaf electroscope. No divergence of the leaves took place; but on drawing sparks by the hand or by an earth-wire from the electroscope knob, from Q, or even from T′, a divergence of the leaves took place, rapidly followed by collapse at every spark so drawn, the gold leaves being thrown into a state of violent flutter. If the hand, or earth-wire, were suddenly removed from contact, a residual charge usually remained upon the leaves of the electroscope; and this charge was variously positive or negative, changing sign apparently according to the last oscillation of the secondary discharge.

Experimentation with the electroscope could not be carried on when *w* was removed more than 10 or 12 millims. from T, as the momentary charges received by the gold leaves were so violent as to destroy them.

10. Throughout the above experiments the most curious effects of induction were exhibited by all metallic bodies in the neighbourhood of the apparatus. From any of these within a range of several yards sparks of a similar reciprocating nature could be drawn by bringing near an earth-wire or any conductor of large surface, whether insulated or not.

11. It was found, as in a preceding case stated at the close of § 3, that no sparks could be drawn from Q (fig. 3) when *w* was brought up to actual contact with T. That is, an in-

termittent current (as is that in the secondary wire of the coil) passing through a *closed* circuit does not evoke that kind of disturbance in a neighbouring conductor which is evoked when the intermittent current has to overleap an interval of air, however short. This result proved that the appearance of a momentary charge upon Q when *w* and T were separated was the result of induction from a momentary charge upon P, and not merely from a current passing through P. The well-known phenomenon of the statical charge produced upon the separated terminals of the secondary circuit of an induction-coil will account for the presence of single momentary charges upon P and upon T. These charges must accumulate through a short but definite period of time until they have acquired sufficient density to overleap with a spark the resistance offered by the layer of air *w* T—the density of the accumulating charge depending on the dryness of the atmosphere, the perfectness of the insulation, and the distance between *w* and T. Though this period be very short, such charges will necessarily, by the inductive influence of their presence, disturb the electrical equilibrium of all near conductors such as Q. The equally well-known phenomenon of the return-stroke, investigated by Lord Mahon in 1779, will account for the appearance of a return-spark after an interval perhaps not exceeding the thousandth part of a second, thus establishing the reciprocating nature of the discharges passing between Q and C.

12. In the case of the earlier experiments (§ 2), where an interrupted primary current passes round an electromagnet, similar conditions virtually exist. The extra-current consequent on breaking the primary is a current of high electromotive force, like the secondary current of the coil. It, too, has a sensible interval to overleap, though the distance in this case is not constant. It, too, must accumulate upon its conductor in order to acquire sufficient density to overleap the gap in the circuit. It, too, can therefore, during a distinct minute period of time, analyze the neutral electricity of the electromagnet-core across the dielectric of silk or cotton that insulates the conducting wire therefrom. In this case, too, we have consequently the conditions of a rapidly charged and discharged condenser, giving rise to reciprocating induced sparks.

13. This conclusion can be directly proved by recurring to the earlier experiments (fig. 2) and introducing across the circuit a wire of suitable resistance to short-circuit the extra-current so that it may complete its route without having to overleap the break at the key. This is shown in diagram in fig. 6, where R is a box of resistance-coils introduced between a and a'. If the wire of which the electromagnet E is made be stout, its resistance will be a mere trifle, and a resistance of 3 or 4 ohms at R will be sufficient. In some cases a drop of pure water between the points of contact at K has also the result of obviating the extra-current spark. And in every case, when the conditions are so arranged as to obviate the appearance, on breaking contact, of the extra-current spark at K, no earth-wire, nor any conductor, will draw a spark from the electromagnet-core—a decisive proof that the sparks so drawn were due to induction by the statical charge of the accumulating extra-current, and to that alone.

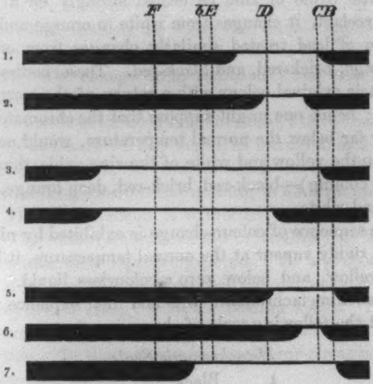
VIII. *Selective Absorption.* *By* WILLIAM ACKROYD.

AT present much attention is being paid to absorption-spectra for technological as well as purely scientific reasons; but in the absence of classification and of a general theory accounting for the facts observed, the whole subject is surrounded by a haze which it were well for progress to dispel. Much perplexity and not a few mistakes have arisen from the confusing of two kinds of absorption, or at least two different manifestations of the same phenomenon, which hitherto have not been sufficiently contradistinguished. These we propose to classify on the basis of the following typical experiments.

1. Light is transmitted through a thin layer of potassic dichromate at the normal temperature, and again at a little below its fusing-point. We obtain spectra approximately represented by Nos. 1 & 2. It will presently be shown that this increase of absorption at the higher temperature is the result of structural alterations in the dichromate. We shall therefore call this kind of absorption *structural absorption.*

2. A glass cell, 15 centims. × 3 centims., contains cupric

sulphate in solution. Light sent through the 3-centims. direction gives spectrum No. 3, whilst light transmitted through the 15-centims. direction gives spectrum No 4. We have here increase of absorption without any structural alterations in the absorbing medium; for the cupric sulphate remains the same during the two observations, and the temperature is unaltered. The only difference is one of extent of medium. For this kind of absorption we propose, at the suggestion of Dr. Guthrie, the term *transverse* absorption.



Professor Gladstone*, when speaking of the action of heat on coloured solutions, thus tacitly refers to the two kinds of absorption:—"The elevation of temperature seems merely to heighten the absorbent power of the dissolved salt, so that light absorbed by a certain quantity of the heated solution is the same as would have been absorbed by a larger quantity of the same solution if cold." Notwithstanding this, the two kinds of absorption seem not to have been formally separated; and the mixed inferences from one and the other have naturally produced a confusion in the minds of students which has made selective absorption a subject little understood. We shall confine our observations to structural absorption.

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* Phil. Mag. [IV.] vol. xiv. p. 423.

Structural Absorption.—Alteration of structural absorption upon elevation of temperature is, as a rule, obvious to the eye as a change of colour. This colour-change, for which I have elsewhere proposed the name of metachromatism, has been studied by Schönbein, Gladstone, Houston and Thompson, and, lastly, by myself. Many theories have been offered to account for the phenomenon; these were discussed in my paper on Metachromatism*, read before the Chemical Society on the 3rd of February last.

If a little oxide of zinc be heated strongly on a piece of white porcelain, it changes from white to orange and yellow. Chromate of lead treated similarly changes from orange to deep orange, brick-red, and black-red. These bodies quickly regain their original colour with a return of the normal temperature; hence one might suppose that the chromate of lead, if cooled far below the normal temperature, would acquire in succession the yellow and white of the zinc oxide, thus (in the order of cooling)—black-red, brick-red, deep orange, orange, yellow, and white.

Such a sequence of colour-change is exhibited by nitric peroxide; a ruddy vapour at the normal temperature, it becomes orange, yellow, and below zero a colourless liquid. From a study of such metachromatic facts and their sequence we have arrived at the following scale of change:—

Metachromatic Scale.

Heating or expanding.	↑	Scale	↓	Cooling or contracting.
		Black Brown Red Orange Yellow Green Blue White or Colourless.		

The scale may be illustrated by heating the following anhydrous bodies on white porcelain. Zinc oxide changes from white to yellow and orange; metaborate of copper from blue to green and yellowish green; baric chromate from yellow to orange; mercuric oxide from orange-yellow to orange, red, and brown; potassic dichromate, red to dark red; trimanganic tetroxide, reddish brown to nearly black; and cuprous oxide glass from scarlet to dark scarlet and black.

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* Chemical News, vol. xxxiv. pp. 76, 77.

Respecting this colour-change, we make out:—(1) that it arises from increased structural absorption with elevation of temperature, the more refrangible increment increasing at a greater rate than the less refrangible; and (2) that the only necessary concomitant is alteration of atomic potentiality—a change from the white towards the black end of the metachromatic scale signifying atomic recession, and a change from the black towards the white end, atomic approach.

(1) In support of this we must refer to the bichromate experiment. The change from red to dark red viewed spectroscopically gives spectra Nos. 1 and 2.

(2) To arrive at the approximate cause, I have heated colour-changing bodies in various media, as nitrogen, carbonic anhydride, and hydrogen, the result of which has been to show that the surrounding medium has nothing to do with metachromatism. The phenomenon is exhibited by all three states of matter—by solids (amorphous and crystalline), by liquids, and by gases near their liquefying-points. By a process of elimination it may readily be seen that the phenomenon is due to the reception of energy from the heating agent. Now of this transferred kinetic energy a portion is converted into energy of position. In the metachrome or colour-changing body we have therefore—

i. Kinetic energy, and the complementary.

ii. Potential energy. This energy of position is acquired by

  α. The overcoming of cohesion (molecular recession or molar expansion), as, *e. g.*, in the conversion of ice into water, and water into steam, *work which is accompanied by a change of density.*

  β. The overcoming of chemical attraction (atomic recession or molecular expansion), which finally ends in decomposition, as, *e. g.*, in the resolution of $PtCl_4$ into $PtCl_2$ and Cl_2.

I. Now metachromatism is not confined to the coloured bodies one meets with in the laboratory; for many anhydrous silicates exhibit colour-change, and in some the change is permanent after the metachrome has been subjected to a high temperature. This is shown in the following Table* in each example save that of olivine.

		Density before ignition.	After ignition.	
1. Olivine	Pistachio-green	3·389	Pist.-green	3·378
2. Beryl	Straw-yellow	2·697	Blue	2·697
3. Topaz	Sherry	3·539	Pink	3·533
4. Zircon	Brown	4·515	White	4·540
5. „	Aurora-red	4·863	Colourless	4·863

If we might assume that *two bodies of identical chemical composition and density* have at a common temperature the same amount of kinetic energy, then it is evident that we may eliminate kinetic energy from the list of possible causes. For, to take the beryl (2), we have differences of colour (that is, of structural absorption) at a common temperature, and the same in the zircon 5, without alterations of density or chemical composition.

The behaviour of mercuric iodide is perhaps a less equivocal demonstration of this point. Examined spectroscopically at (say) 16° C., a band of red light is transmitted extending from B to D. This narrows as the temperature rises (in other words, there is an increase of structural absorption), up to about 140° C. The band of transmitted light now suddenly widens and extends to a little beyond *b*. Spectra Nos. 5, 6, and 7 illustrate this change. After the decrease of absorption as represented by No. 7, we have the normal increase with elevation of temperature; but still at 220° C. there is not so much light absorbed as there was at 16° C. Now the heat or kinetic energy of a body increases with elevation of temperature; therefore the deep orange HgI_2 at 220° C. has more kinetic energy than the red modification at 16° C.; but the latter has greater structural absorption. The rule is that increase of kinetic energy is accompanied by increased structural absorption. In the behaviour of mercuric iodide we have the opposite of this, viz. decrease of absorption with increase of kinetic energy, whence we infer that the change of absorption which characterizes metachromatism is not necessarily accompanied by change of kinetic energy.

II. Expansion by heat (*i. e.* decrease of density) is an all but universal law so far as we at present know. There are several exceptions, however; and many of these are among the silicates. Their anomalous behaviour is, as a rule, pointed out by the colour-change, as in the case of the zircon. But there may be change of colour, as in the beryl, without alteration of density, *i. e.* without appreciable molecular approach or recession. On the other hand, we have in olivine an example of change of density (molecular recession) without a corresponding alteration of colour. More facts of the same nature might readily be adduced, from which we infer that molar expansion or contraction is not a necessary concomitant of alteration of structural absorption. We have now excluded from our list of possible concomitants i. and ii α. Hence it would appear that ii β is the only necessary concomitant—a conclusion which receives strength when we consider that the gradual increase of structural absorption in such bodies as HgO, $PtCl_4$, and $Cr_2\,O_5\,Ko_2$ terminates with their resolution into lower compounds, or into their constituent elements.

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* Compiled from "Some Experiments on the Density of Garnet, &c." (Church), Chem. Soc. Journ. vol. xvii. pp. 386 & 415.

Relation of Colour to Density.—An attempt was made in 1765 by Delaval to show the connexion between colour and density. In a paper read before the Royal Society, he observes[*] :—"It appears from Newton's experiments that denser substances ought by their greater reflective power, in like circumstances, to reflect the less refrangible rays, and that substances of less density should reflect rays proportionably more refrangible and thereby appear of several colours in the order of their density." The seeming success of this attempt is perhaps due to the comparative nature of his facts; for he compares coloured glasses of each of the following metals in the order of their densities:—gold, red; lead, orange; silver, yellow; copper, green; iron, blue. We can readily see now the error of such a comparison; for the colour of glass must evidently depend upon the state of the metal in it; *e. g.* differently coloured glasses may be obtained from the different oxides of the same metal. To take an instance, whilst the cupric oxide gives a bluish-green glass, we know that the cuprous oxide gives a red one. Nevertheless it will be obvious from our foregoing observations that it is possible to establish a connexion between density and colour as due to structural absorption. Not, however, until we have made out a special relation can we well proceed with certainty to establish a comparative one; nor will this special relation accord with Newton's prediction.

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[*] Philosophical Transactions, vol. lv. p. 10.

From the nature of metachromatism, it is probable that increase or decrease of interatomic distance will in most cases be accompanied by a corresponding alteration of molecular interspaces. Hence in allotropes we shall look for exactly the opposite of what Delaval sought to establish, viz. for cold colours with great density and warm ones with low density.

Metachromatic scale.	Carbon.	Sulphur.	Topaz.	Titanic oxide.	Zircon.	Argentic iodide.	Calcic fluoride.
Black	Graphite, 2·35						
Brown	......	Ductile, 1·957	......	Brookite, 4·085	Brown, 4·515		
Red	......	......	Pink, 3·533	......	......	Dark red, 5·406	
Orange							
Yellow	......	Octahedral, 2·05	Yellow, 3·539	Rutile, 4·283	......	Yellowish green, 5·681.	
Green.........							
Blue	......	......	......	......	......	......	Blue, 3·170
White or Colourless	Diamond, 3·33	......	......	......	White, 4·540	......	White, 3·176

The fact of phosphorus being an exception does not militate against this relation, since it is highly probable that the other anomalies of this body will receive elucidation when studied from the metachromatic standpoint. The change in colour of mercuric iodide, which we have already referred to, indicates atomic approach; and to ascertain whether this is accompanied by a corresponding molecular motion and consequent change of density has been the object of a large number of experiments. From the peculiar difficulties encountered, however, as yet I have obtained no trustworthy results.

The next step from the special relation we have pointed out to one of a comparative nature would seem to be in an extension of the following law of colour-sequence:—"In a series of anhydrous binary compounds of the same two elements, those which have the highest amount of the basylous element exhibit the least structural absorption; and, *vice versâ*, those which have the least amount of the basylous element have the most structural absorption"*.

The Five Orders of Spectra.—In the borderland between chemistry and physics, data are being accumulated which tend to make the former a dynamical science. Not the least important of these data are those which furnish us with the connexion between the different kinds of spectra. Professor Roscoe is of opinion† that there is not sufficient evidence as yet to support the sequence in the five orders proposed by Lockyer‡ and now generally received; and in the light of metachromatism it may be necessary to modify this sequence. The juxtaposition of the orders constituting a class of spectra we take to be founded upon that merging of the optical characters of one order into those of another which is exhibited when the molecular changes in the radiating or absorbing body cause such optical alterations. Now confining our attention to low-temperature or absorption spectra, it is evident from what has already been said that change in structural absorption alone is available for forming a sequence of orders. Hence we consider the fifth order, as at present received, misplaced, the *unique continuous absorption* being from the nature of the experiment a transverse absorptional effect.

A sequence of orders will readily suggest itself if we keep in mind that change in absorption to which metachromatism is due. Conceive of a colourless body capable of undergoing the whole series of change. It first reflects or transmits rays of every refrangibility; as absorption increases, the band of transmitted or reflected light gradually narrows and becomes less intense; finally the field is darkened and we get continuous absorption. What we propose, then, is shown in the following comparison, made in order that the student may have a clearer conception of the matter.

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* Chemical News, vol. xxxiv. p. 76.

† Watts's Dictionary, 2nd Supplement, p. 1093.

‡ Proceedings of the Royal Society, June 11, 1874.

Now received.		What we propose.
1st order	Line spectra	Class I. Radiative.
2nd order	Channelled-space spectra	
		Class II. Absorptive.
		1. Continuous absorption.
3rd order	Continuous absorption at the blue end..........	2. Partial absorption, *i. e.* absorption at the blue and red ends, or at any intermediate part of the spectrum.
4th order	Continuous absorption at the red end	
5th order	Unique continuous absorption	3. Continuous spectrum.

Class II. 1, 2, and 3 constitute the metachromatic scale. To illustrate the bridging over of 1 and 2 no simpler experiment could be tried than the following. Take a piece of copper wire and cover with suboxide by gently heating over a Bunsen burner. Fuse the covered wire into a capillary glass tube. A scarlet glass is thus obtained which is black whilst hot, *i. e.* exhibits continuous absorption (1), and scarlet whilst cold, exhibiting partial absorption (2). 2 and 3 are bridged over by a host of bodies like ZnO. When hot they, as a rule, exhibit absorption at the blue end of the spectrum (2), but when cold they are white or colourless (3).

Respecting the merging of Class I. into Class II. nothing much at present can be said, since questions are involved which require further investigation.

IX. *On a Mechanical Illustration of Thermo-electric Phenomena.* By OLIVER J. LODGE, *B.Sc.*

[With a Plate.]

THE publication of the following speculation requires an apology. It is in continuation of a paper on a Mechanical Illustration of Electric Induction and Conduction, published in the November Number of the 'Philosophical Magazine;' and the sections are numbered on continuously with those in that paper; but whereas the mechanical analogies suggested in the former part of the paper are useful as mere analogies even if they do not (as I believe they do) throw some light on the actual molecular processes, the present portion contains nothing of sufficient mechanical simplicity to be of much service as mere illustration, and it therefore has little value unless the imaginary mechanical actions are really analogous to those which actually do produce thermo-electric currents. I have accordingly laid it aside for a couple of months to see if any thing would occur to show the improbability of this being the case; but as any fresh light has appeared rather to confirm than to weaken the hypothesis, I now venture to publish it. But it is necessary to say that, though the hypothesis does, with the help of a few more or less reasonable assumptions, account for all the known phenomena of thermo-electricity, yet it is quite possible that the assumptions made are not the most likely ones, and that the laws deduced are not exactly the true ones. Nevertheless, since they fulfil the necessary conditions as well as the true ones, they are sufficient to show that a consistent account of the facts can be given by means of a hypothesis founded on a connexion between the molecules of matter and electricity which is called "resistance" and which is known to exist, though it is not yet accounted for.

I have preferred to continue speaking in terms of the mechanical model, because discussions concerning molecules and æther are apt to have in appearance the looseness which they very often possess in reality. Moreover one has the advantage of being able to leave the precise relation which the cord is to bear to electricity or to the æther, and which the buttons are to bear to molecules, as well as the real nature of the connexion between the buttons and the cord, unspecified and open to any definition which the vortex theory of matter may suggest.

§ 21. In a communication to the 'Philosophical Magazine' for November 1876 (p. 353), the passage of electricity through dielectrics and electrolytes was illustrated by mechanical analogies at some length, but its passage through ordinary metallic conductors (§ 11) was only touched upon sufficiently to enable them to be compared with the other media, and all the details of the process were left unconsidered. In the present paper it is intended to enter into these details; and it is to be regarded as a continuation of the first paper.

The electrical resistance of a metal was represented by the friction to which a cord was subject in passing through a row of nearly smooth buttons fixed to a rigid support (see fig. 3, Plate II.). The cord when moving represented a current of electricity; and the buttons represented the molecules of the conductor. But, since we were not supposing the conductor to be at the absolute zero of temperature, the buttons properly ought not to have been standing still but to have been executing some kind of periodic motion.

Let us then suppose that the rods supporting the buttons are not perfectly rigid, but highly elastic, and that each button is vibrating backwards and forwards in the direction of the length of the cord with a succession of harmonic motions of short period and very small amplitude. Each button will by its friction tend to move the cord with it. Being all exactly alike, their vibrations will all be isochronous; but they will be in all manner of phases at any one instant; so on the average they will neutralize each other's effect on the cord, and the cord will remain stationary without oscillation.

The hypothesis just made, viz. that the molecules of a solid are oscillating, and that the oscillation of any one exerts a certain electromotive force, capable of producing a current except for the circumstance that it is exerted equally in opposite directions in rapid succession, and moreover that it is in general neutralized by the similar but ill-timed action of its neighbours, is the hypothesis whose consequences it is the object of the present paper to trace.

§ 22. First of all, then, there is some energy lost in this motion; for the buttons are sliding backwards and forwards on the cord, and, though they are tolerably smooth, the friction must ultimately bring them to rest, unless the loss of energy is made up to the body from other portions of the same body or from external sources. The energy which is thus continually being wasted in warming the cord must, I think, be held to correspond to the heat lost by radiation into space; the loss being compensated, in cases of equilibrium of temperature, by equivalent receipts from neighbouring bodies. But if a set of molecules, or a finite mass of any substance, be isolated from all other bodies and left to itself in free space, the molecules will gradually deliver up their motion to the interpenetrating medium, and will ultimately come to rest. If, then, we calculate the work done in unit time by a button sliding to and fro on the cord, we shall get the rate at which a body cools under these circumstances; and from this the rate under any other circumstances can be obtained at once by simply subtracting the rate at which it gains heat from the enclosure.

Since we have no data regarding the actual motion of a button, we may as well for the present consider it as simply harmonic; any other sort of motion will give very nearly the same result. Let the period of the simple harmonic motion of a button be $2t=\frac{2\pi}{\sqrt{\kappa}}$, and let its amplitude be a, so that $2a$ is the whole length of a button's excursion from right to left. Its velocity at any distance x from its mean position is $v=\sqrt{\kappa(a^2-x^2)}$, and its maximum velocity is $V=a\sqrt{\kappa}$. Now we remember that the retarding force acting between a button and the cord is proportional to r the specific resistance of the substance or the coefficient of "friction," and to v the velocity of the button on the cord at any instant (this is Ohm's law; see § 9 equation (1) and § 10); hence the work done in one excursion from right to left is

$$W=\int_{-a}^{+a} rv\,dx=\frac{\pi}{2}ra^2\sqrt{\kappa}.$$

The work done in unit time is therefore

$$\frac{W}{t}=\tfrac{1}{2}ra^2\kappa=\tfrac{1}{2}rV^2; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this is the rate* at which a button loses its energy when left to itself without assistance from others, or the rate of cooling of a substance placed in an enclosure at absolute zero. Hence, assuming that the absolute temperature θ is connected with the maximum velocity V and the atomic weight m by the relation

$$\tfrac{1}{2}mV^2=s\theta,$$

the rate of cooling is given as

$$\dot{\theta}=\frac{s}{Jm}r\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which would be simply proportional to θ (Newton's law), except that the resistance r itself varies with the temperature.

§ 23. The above conclusion that the radiating power of a body is directly proportional to its specific electrical resistance and inversely as its atomic weight, is not negatived by the experiments of Leslie, and of Provostaye and Desains, as far as they go; for Leslie's order of the metals in radiating-power agrees nearly with their inverse order in conductivity. Moreover, if one finds the value of the expression $\frac{m\dot{\theta}}{r\theta}$ for the few metals more accurately experimented on by Provostaye and Desains, one gets a number whose constancy is indeed rough but quite as good as could be expected. The only metals apparently whose radiating-powers were ascertained by them were platinum, copper, gold, and silver; and of these gold was only tried as gold-leaf, which is scarcely a fair test, because radiation is more than a surface action. The following Table contains in the first column a mean value of the radiating-power, taken from Ganot, art. 364, for the three metals, silver, copper, and platinum (gold is left out because its results are discordant); the second column contains the relative atomic weights; the third column an approximation to the relative electric conductivity of each metal, obtained by taking a mean between the value given by Matthiessen and that given by Becquerel (Miller, vol. i., being my authority); and the last column contains the numbers which ought to be constant.

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* If, instead of assuming a simple harmonic motion, one takes any motion having average velocity $\frac{2}{\pi}V$, the rate of doing work will be nearly $\frac{4}{\pi^2}rV^2$, which is only slightly different from (1).

	$\dot{\theta} : \theta$.	m.	$\frac{1}{r}$.	$\frac{m\dot{\theta}}{10r\theta}$.
Silver	2·7	108	100	2916
Copper	4·9	63·5	96	2987
Platinnm	10·1	197	13	2586
Gold	4·3	196	71	5985

Taking 2850 as a rough mean value of this constant, one can calculate backwards to the radiating-power for any metal on the same scale. The following Table contains the radiating-power given by the hypothesis for a dozen common metals, most of whose resistances at 0° Centigrade were ascertained by both Matthiessen and Becquerel. The exclamatory mark against gold signifies that its atomic weight has been called 98 because the correct value 196 gives 2·0, which is apparently too small a result.

Metal.	Mean conductivity at 0° C.	Radiating-power at zero Centigrade.
Silver	100	2·6
Gold!	71	4·1
Copper	96	4·7
Cadmium	24·1	10·6
Platinum	13	11·1
Zinc	26·5	16·5
Lead	8·3	16·6
Tin	13·2	18·3
Iron	14·6	34·8
Antimony	4·6	50·8
Mercury	1·7	83·8
Bismuth	1·25	108·6

Concerning this Table, I have to remark that the hypothesis cannot be expected to give correct values for the last three metals; for the electrical resistance was ascertained by experiment on large masses of material, whereas it is the *molecular* resistance which is concerned in radiation; and though the two are the same in homogeneous material, the experimental value of the resistance is probably too great in the case of crystalline metals like antimony and bismuth, or even perhaps iron. And as regards mercury, its molecular motions cannot be all oscillatory like those assumed in the hypothesis, but must have much of their energy in the form of whatever motion is characteristic of liquidity.

§ 24. Now the researches of Dulong and Petit have indicated the true law of cooling to be

$$\dot{\theta}=p(a^{\theta}-1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p is a constant depending on the nature of the substance, and a is a number usually stated to apply to all substances and to be equal to 1·0077. As, however, this is only an experimental number, I shall take the liberty of assuming that in general both p and a vary with the substance, but that the value of a is always very close to unity.

Equations (2) and (3) combined give us the law according to which the electrical resistance of a body varies with the absolute temperature, viz.:—

$$r=\frac{\mathrm{J}mp}{s}\cdot\frac{a^{\theta}-1}{\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

I shall denote the constant $\frac{Jmp}{s}$ by the letter h for shortness, and shall occasionally use (4) in the expanded form—

$$r=\alpha+\beta\theta+\gamma\theta^2+\dots, \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\alpha=h\log a, \quad \beta=h\frac{(\log a)^2}{2\,!}, \quad \gamma=h\frac{(\log a)^3}{3\,!}, \text{ \&c.}$$

The series is very converging, because a is so near 1; thus if $a=1\cdot0077$, $\log_e a=\cdot0076$; and the first two terms will in many cases suffice.

Digression.

§ 25. In Balfour Stewart's 'Heat,' page 207, it is shown from the theory of exchanges that the internal radiative power of a transparent substance is proportional to the square of its index of refraction, because a small cone of rays issuing normally from some small area inside the body will spread out at the surface into a cone of larger angle, the ratio between the two solid angles being obviously μ^2, so that to maintain equilibrium of temperature the internal radiative power must be μ^2 times that of the surface of the enclosure exposed to the plane surface of the body. There is no ground for denying an index of refraction to metals (cf. Professor Ketteler in the November Number of the 'Philosophical Magazine,' p. 333); so we will suppose the same to hold good with them.

Again, the velocity of light in a medium (*other things being equal*) will be proportional to the square root of the elasticity of the threads joining the buttons (§§ 8 and 18); for the maximum velocity V of a particle is $a\sqrt{\kappa}$ (§ 22); and this is related to the velocity of propagation of light L by the equation

$$V : L = 2\pi a : \lambda,$$

λ being of course the wave-length, whence

$$L=\frac{\lambda\sqrt{\kappa}}{2\pi}.$$

But the velocity of light in a medium is known to be inversely as μ; therefore

$$\mu^2 \propto \frac{1}{\kappa} \propto K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(see § 8), which appears to agree with Maxwell's theory that the index of refraction of a substance is nearly equal to the square root of its specific inductive capacity K.

We have found, then, that the internal radiating-power, which we have shown to be proportional to r, is also inversely proportional to κ, because directly proportional to μ^2; hence

$$\kappa \propto r^{-1}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or conductivity for heat and electric conductivity in metals are proportional to one another (for we saw in § 18 that κ was probably proportional to the conductivity for heat); and therefore the conductivity for heat varies with the temperature according to the law

$$\kappa = \frac{g}{h} \cdot \frac{\theta}{a^\theta - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which is a curve not very different from $\frac{1}{\theta}$. It vanishes for $\theta = \infty$, and it becomes great and equal to $\frac{g}{h \log a}$ for $\theta = 0$.

The law of the steady conduction of heat parallel to the axis of x through a slab is

$$\frac{d\text{Q}}{dt} + \kappa \frac{d\theta}{dx} = 0.$$

Now Professor Tait, in his 'Recent Advances in Physical Science,' p. 271, says that when every thing has attained a permanent condition, the available energy would have a minimum (and therefore a stable) distribution if the temperature fell along a logarithmic curve, or if $\frac{d\theta}{dx} \propto \theta$; it is therefore to be assumed that this is the case. But from this it follows, since $\frac{d\theta}{dt} = 0$, that the *thermometric* conductivity $\frac{\kappa}{\sigma}$ must vary inversely as the absolute temperature. κ by itself nearly does, but not quite, (8); so we get a law for the variation of specific heat per unit volume with temperature, viz.

$$\sigma \propto p\kappa\theta = \frac{\text{H}}{m} \cdot \frac{\theta^2}{a^\theta - 1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is tolerably constant, or the curve runs almost parallel to the axis of θ, for ordinary ranges of temperature; it attains a maximum about when $\theta = \frac{2}{\log a}$, and it has points of inflexion about when $\theta = \frac{2 \pm \sqrt{2}}{\log a}$, the three temperatures referred to being $-196^\circ{\cdot}4$, $-10^\circ{\cdot}8$, $+174^\circ{\cdot}8$ Centigrade, if the value of a were 1·0077 ; but a very small change in a would obviously cause great alteration in these temperatures.

One may write a tolerably close approximation to σ for ordinary values of θ thus:

$$\sigma \triangleq \frac{6\mathrm{H}}{m\,(\log a)^2} \cdot \frac{1}{(3+\theta \log a)}. \quad . \quad . \quad . \qquad (10)$$

I have put p into (9) with no other justification than to get rid of it from κ (whose h contains it) so as to leave nothing but the atomic weight m in (9), except a universal constant H, this H being proportional to $m\sigma$, the atomic heat.

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§ 26. In saying, as we did in § 21, that the cord remains stationary under the combined oscillatory motions of the buttons, we have assumed that the friction of a button is symmetrical as regards right and left ; that is, we have assumed that the buttons are not notched so as to be rougher when sliding over the cord one way than when sliding the other way, as an ear of rye-grass would be. If this condition were not satisfied, the simple to-and-fro oscillations of the buttons would confer a progressive motion on the cord. Possibly the condition is not satisfied in some crystalline bodies, like tourmaline: and this would account for their internal polarity; for since the crystal is an insulator, the cord will be displaced by the unequal friction only so far as the dielectric elasticity will permit it, and the result will be a state of strain inside the crystal and a difference of potential between its opposite faces. In time the potentials of these faces would become equalized by surface leakage or otherwise; but any quickening of the motions of the molecules (rise of temperature) will increase the electric displacement and strain, and will restore a certain amount of difference of potential to the faces. On the other hand, a lowering of the temperature of the crystal will give the elasticity an advantage over the friction ; some of the previously displaced cord will return, and the potentials of the faces will change sign.

§ 27. Return now to the consideration of a simple metallic conductor with its buttons all executing isochronous simple harmonic motions on the cord. Apply a force to the cord so as to make it move continuously forward with a velocity u; that is, generate a current of strength proportional to u in the conductor by means of external electromotive force. We will not suppose that u is great enough at all to interfere with the motion of the buttons; in other words, we will assume that u is incomparably less than V; nevertheless the vibrations of the buttons, though unaltered in space, are no longer symmetrical right and left with respect to the cord: in one direction their relative velocity is the sum, in the other the difference of their respective velocities; hence the motion of the cord is resisted, and work must be done to drive it. If the buttons were stationary, the force opposing the motion of the cord in each button would be ru by Ohm's law; and this force is unaltered by the motion of the buttons so long as u is small. For consider the work done by a button in one excursion; properly speaking it would be

$$W=\int_{-(a\pm\frac{1}{2}ut)}^{a\pm\frac{1}{2}ut}(v\pm u)r\,dx, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the signs to be taken according as the excursion is against or with the cord; but as this expression is unmanageably long, I will be content with the simpler one, true when u is small,

$$W_1=\int_{-a}^{+a}(v+u)r\,dx=\frac{\pi}{2}ra^2\sqrt{\kappa}+2aru$$

for the work done by a button in an excursion against the cord, and

$$W_2=\int_{-a}^{+a}(v-u)r\,dx=\frac{\pi}{2}ra^2\sqrt{\kappa}-2aru$$

for the work done in an excursion with it. The balance of work done against the cord in a double excursion (that is, while the button travels over a distance $4a$) is

$$W_1-W_2=4aru\,; \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

hence the average force exerted must be equal to ru.

The rate of *radiation* work of a button is

$$\frac{W_1+W_2}{2t}=\tfrac{1}{2}ra^2\kappa, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the same as that given by equation (1) when no current was passing.

We have found, then, that each button exerts an average force on the cord equal to ru; hence, if there are n buttons in a row on each cord, and m cords lying side by side, the electromotive force or difference of potential required to drive a current of strength $mu = C$ through a conductor of sectional area represented by m, and length represented by n, is

$$\frac{F}{m} = E = nru = \frac{n}{m} r \, . \, mu = RC, \quad . \quad . \quad . \quad (14)$$

which merely shows that Ohm's law, if true for each button, is true for the whole conductor if its temperature is kept constant. The work done by this force in any time T will be equal to the product of the force into the distance through which it may have moved the cord in that time—that is, FuT; hence the rate of "frictional" generation of heat by the current is

$$jmnru^2 = jRC^2, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is Joule's law that the amount of heat generated in a given time is proportional to the resistance of the conductor and to the square of the strength of the current. It is convenient to use j for the number of units of heat contained in a unit of work, *i. e.* for the reciprocal of J.

Though I have here taken account of more cords than one, it will not be necessary to do this hereafter, as what is true for any one cord will be true for any number, so we will henceforth consider $m = 1$.

§ 28. So far we have considered only homogeneous circuits, in which all the buttons have the same amplitude, the same period, and the same average velocities. In these cases the cord is in equilibrium under the united and balanced action of all the buttons on it, but it is perfectly free and capable of permanent displacement by the slightest force; so that if even one button were made to move forward always faster than it returned, it would exert an electromotive force on the cord and move it forward a little at each oscillation. On the other hand, if any button be made to go forward more *slowly* than it returns, it will exert less force on the cord than is expected of it, and the cord will be moved backwards by the other buttons while the slow one is going forward. Hence if we conceive a cord on which all the buttons but one are oscillating regularly to and fro with the average velocity v, while this one is oscillating forwards with velocity $v+x$ and backwards with velocity $v-x$, then the cord will be pushed forward *both* by reason of the too rapid motion and by reason of the too sluggish one; and the electromotive force urging it is

$$(v+x)r-(v-x)r=2xr. \quad . \quad . \quad . \quad . \quad . \quad (16)$$

If the cord were allowed to move, the work done per second by this force would be $2xru$; and j times this is therefore the rate at which heat is absorbed at such a point by this force. The heat so absorbed is evolved in other parts of the circuit, because friction opposes the motion of the cord with a force nur equal to $2xr$. If we urge the cord at any rate u through such a circuit by an external electromotive force E acting in the same direction as the force of the x-button, the work done per second is

$$\mathrm{E}u=(nur-2xr)u,$$

or the heat generated is

$$j(nu^2r-2xru), \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and the strenth of the current is

$$u=\frac{\mathrm{E}+2xr}{nr}=\frac{\mathrm{E}+\Pi}{\mathrm{R}}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Now (17) contains two terms, one depending on the square of the current and being the irreversible frictional generation of heat (15), and the other changing sign with the current and representing the heat absorbed or generated at the x-button according as u is positive or negative, remembering that the current has been considered positive when going the way the button tends to drive it.

Something analogous to the unsymmetrical action of this x-button is what I imagine to go on at a junction either of two different metals at the same temperature, or of two parts of the same metal at different temperatures; and accordingly $2jxru$ will correspond either to the Peltier effect or to Thomson's *convection* effect; and $2xr$ is analogous to the coefficient which is called Π in the one case and may be called Θ in the other.

§ 29. Let us now proceed to consider what kind of unsymmetrical motions may reasonably be expected to actually occur at a junction either of two different metals at the same temperature, or of two portions of the same metal at different temperatures. In both cases the molecules on the two sides of the junction are vibrating at different rates:—in the first case so that

$$m_a v_a^2 = m_b v_b^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

m_a and m_b being the atomic weight of the two metals; and in the second case so that

$$\theta_2 v_1^2 = \theta_1 v_2^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

θ_1 and θ_2 being the absolute temperature on either side of the junction.

Now it is very unlikely that the vibrations of the closely packed molecules of a solid should be any thing so simple as the simple harmonic motions partially assumed in §§ 22 and 27: in other words, the restoring force cannot be due simply to bending of the connecting rods, but it must also be an effect of the neighbouring buttons by impact or otherwise. Any button in the interior of a mass of metal will be driven backwards and forwards with a velocity depending on the average velocities of the buttons in its neighbourhood as well as on the elasticity of its connecting rods; and if the mass be homogeneous, its velocities to right and left will be equal. But consider a button on the bounding surface of a mass in vacuum. It is being struck behind continually by its contiguous buttons, but there is nothing striking it in front; and accordingly its velocity in the excursion outwards will be greater than in its return journey, the return having to be accomplished by the strained rods in opposition to the force of impact. Any cause which either increases the average velocity of the molecules or decreases the elasticity of the rods will increase the difference between the out and in velocities, which may be said to depend on v directly and on $\sqrt{\kappa}$ inversely. Now a rise of temperature does both these things; it increases v in proportion to $\sqrt{\theta}$, and it decreases κ in the proportion of $\frac{1}{\theta}$ (see (8)); hence the difference of velocity may without violence be assumed to be simply proportional to the absolute temperature in any given medium. As the temperature rises, then, a surface molecule will go forward more and more rapidly and return more and more slowly;

moreover its mean position will be shifted more and more outwards: occasionally a molecule may get struck away altogether, which is evaporation.

If we bring a second mass of the same material at the same temperature into close contact with the first mass, the surface-buttons of each will drive one another inwards, and they will oscillate like any other buttons in the interior of a homogeneous mass. But if the second mass of metal be either of different material or of different temperature from the first mass, its molecules will not be oscillating at the same rate; and though the surface-buttons of each will be partially restored to their places and made to oscillate more uniformly than before, yet, since the impacts of one are more violent than those of the other, they will still have some irregularity—those of the hotter metal A going faster from A towards B and slower in the reverse direction, while those of B go slowly from B to A and faster back again from A to B. On the whole, then, we have a *double* layer of buttons oscillating quicker in one direction, viz. A B, than the other *; and such buttons, if threaded on a cord, would have a tendency to drive it in the direction A B, as we have already seen, § 28.

§ 30. At a junction of two metals, or of unequally hot pieces of one metal, we appear then to have found an electromotive force acting in one direction; but there is something further to be noticed yet. We found in the former paper that in any complete model it was necessary to have not one cord but two, arranged side by side and connected so that however one moves the other must move with the same velocity in the opposite direction—one representing a current of positive, the other the simultaneous equal opposite current of negative electricity. Now the electromotive force whose existence we have been recently imagining, is one that will act on both these cords; and if it acted on both equally they would be both urged equally in the same direction, and consequently could not move at all. It is necessary, therefore, to assume that the bite of the buttons on one of these cords is greater than their bite on the other; but whether it is the positive or the negative cord on which the greatest force is exerted in a given case will depend on the nature of the metal, and possibly also on its temperature—though we have no evidence as regards the latter point, and I shall not assume it.

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* Although we should have at such a junction molecules travelling quicker in one direction than the other, there will be no excess of momentum either way as was to be expected in dielectrics and electrolytes (see § 8 footnote and § 16); for there will be a large number of molecules side by side in such a layer, and, since each takes a longer time over its slow journey than over its quick one, there will be at any instant more molecules moving slowly than quickly, and their excess in number will make up for their defect in velocity, so that the average momentum each way will be the same. But it is a suggestion of Mr. G. Johnstone Stoney's, which he made at the Physical Society last November, in connexion with his theory of Mr. Crookes's radiometer, that though mv may equal $m'v'$ it by no means follows that $\frac{1}{2}mv^2=\frac{1}{2}m'v'^2$: there will, in fact, in the above arrangement be an excess of kinetic energy in favour of the quickly moving molecules, *i. e.* from A to B. This is energy which can be expended in driving the cord. But if the cord be forcibly held so that it cannot move, the energy will still, I suppose, be transferred from A to B; but it will not now be doing useful work, it will be degraded into mere diffusion of heat.

What we have now assumed amounts to this, that the quantity r, called the specific resistance of a substance, is made up of two parts, such that $r=r'+r''$, whereof r' is the specific resistance referred to positive electricity, and r'' is the specific resistance referred to negative electricity, and that in any metal in which a current exhibits *convective power for heat* the two parts are not equal. If the "specific heat of vitreous electricity" is positive (as Thomson has experimentally proved it to be in copper), r'' is greater than r'; but if it is negative (as it is in iron), then r' is greater than r''. However, this will appear more fully presently, § 35.

§ 31. Consider now the electrical condition of a homogeneous mass of metal. Its surface molecules are moving more quickly outwards than inwards, and are hence straining the cords outwards (which cord they strain most depends upon circumstances; but for simplicity I will suppose that there is only one, and that the positive cord): the cord inside is thus in a slight state of tension, or (§ 1) the potential of the metal is lower than that of the air in its neighbourhood. The cord does not move, because the surface forces are balanced all round: it resembles a drop of water in a capillary tube. (If the negative cord were acted on most, the condition of the metal would resemble mercury in a capillary tube, or simply a drop of water in its own skin.) Another mass of different material will show the same thing, only to a different amount. If the two metals are put into contact, we have three kinds of bounding surfaces, viz. those which separate air and A, A and B, B and air; and the forces at each surface are in general different: hence the forces all round A are no longer balanced, and the cord moves, say from A to B, a certain limited extent, just as the water in two capillary tubes of different bore would when they are brought into contact. The particles of the dielectric outside (being also threaded on the cord) will at the same time be pulled nearer to A and pushed further from B; that is, §§ 1 and 2, the surface of A is charged negatively and that of B positively.

§ 32. The difference of potential produced by the above surface-action is closely allied to Volta's contact electricity, which is also an effect taking place at the free surfaces of the two metals, but which is probably greatly assisted by an incipient voltaic current taking place through the air which acts as the exciting fluid, the electromotive force being produced by the tendency of the air to unequal chemical action on the two metals. Since the air is a dielectric and not an electrolyte, there is no continuous current developed, but only a difference of potential capable of causing a current if the resistance of the air were diminished sufficiently; and the cord is displaced through the air and across the junction of the two metals to an extent proportional to this difference of potential, the electromotive force being balanced by the slight state of strain which is set up in the air by this displacement. The metals which show the greatest effect are those which stand furthest apart in the voltaic series.

But the contact electricity spoken of above as generated at the junction of two metals has nothing to do with chemical action. It is an incipient thermo-electric current taking place across the junction, which only shows itself as a slight displacement of the cord, unless the metallic circuit is completed by a second junction generating an electromotive force different from that of the first. The action between zinc and copper would not be at all so strong as between bismuth and antimony: in fact, the metals stand here in their thermo-electric order. Of course, what is actually observed in any ordinary case of two metals in contact is a mixture of the two effects; and the voltaic effect is usually far the greatest.

§ 33. The very provisional value $2xr$ already obtained in § 28 for the electromotive force at a junction is sufficient to show several things. For instance, since it is a direct function of resistance, substances of high specific resistances may be expected to make the best thermo-electric materials—such, for example, as metallic alloys, or sulphides, or, still better, tellurium or selenium*. Hence also we might expect contact effects to be extremely powerful between two substances ordinarily called "insulators." Some violence might have to be used to displace the cord through the very rough buttons of a dielectric; and a certain amount of heat would be generated by the "friction" of the cord through the buttons; but when once displaced it would not easily slide back again, and the effects might accumulate; so that by rubbing a dielectric with a cord-supplying substance (a metal), one could electrify it very highly; and this is done in an ordinary glass electrical machine. Any two substances which differ at all in conducting power may be expected to give some contact-force. Thus, if a crystalline metal conducts better along the fibre than across, or if a strained metal has a higher resistance than an unstrained, or if the conductivity of magnetized iron depends on the direction of magnetization, then contact-force may be looked for in each case at the junction of the substance in its two different states.

§ 34. It is now time to try what are the actual values which the assumptions founded on the model give for the electromotive force developed at junctions, and to see if these values satisfy the conditions which Thomson has laid down for them from thermodynamic principles. Consider, therefore, a junction of two metals A and B, at the temperature θ, whose resistances are r_a and r_b, such that r'_a and r''_a are the positive and negative resistances respectively of the metal A (referring to § 30 for an explanation of these terms), and r'_b, r''_b of B; also let v_a and v'_a be the out and in velocities (§ 29) of the molecules of the metal A, and v_b and v'_b those of the metal B: then the force exerted on the positive cord is

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* Since the resistance of selenium has been found to fall off under exposure to light, it is probable that its "thermo-electric power" will be found to do so also; in other words, illuminated selenium will have a place higher up in the thermo-electric series than unilluminated selenium.

$$F=(v_a-v'_a)r'_a-(v_b-v'_b)r'_b. \quad . \quad . \quad . \qquad (21)$$

Now in § 29 we agreed to consider the difference of the out and in velocities to be proportional to the absolute temperature in any particular metal*: hence we shall have

$$F=A\theta r'_a-B\theta r'_b;$$

similarly for the force acting on the negative cord we shall have

$$F'=A\theta r''_a-B\theta r''_b.$$

Hence the balance of force useful for urging the cords is

$$\Pi=F-F'=\theta\{A(r'_a-r''_a)-B(r'_b-r''_b)\}. \quad . \qquad (22)$$

Now (§ 24) r is of the form $h\frac{a^\theta-1}{\theta}$; and from what was said in § 30 it is plain that h must not only vary for different substances, but must have in general different values for the positive and negative cord in any one substance. Call these values h' and h'', so that $h=h'+h''$. h also changes from one substance to another, and so does a; but I shall assume that the latter is constant as regards the positive and negative cords; if, however, the sign of the specific heat of electricity in a substance were found to depend upon the temperature, then a must also be split into two parts a' and a''. At present I shall only assume that it is different in A and B, and shall call its value in B, b. Putting the values of r into (22), we get

$$\Pi=A(h'_a-h''_a)(a^\theta-1)-B(h'_b-h''_b)(b^\theta-1). \quad . \qquad (23)$$

This is the electromotive force generated at a junction of two metals A and B at the absolute temperature θ; and therefore it is the coefficient* of the Peltier effect; and the heat absorbed per second at such a junction by a current of strength u is (§ 28)

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* The account given in § 29 of the cause of the difference between the out and in velocities at a junction cannot be held to apply satisfactorily to the case of a junction of two different metals; for it makes the thermo-electric power of a metal to depend on the substance with which it is associated, instead of being a simple property of each individual metal and its temperature—as it is known to be, because the metals can be arranged in a thermo-electric series at any temperature. Hence, whatever influence difference of atomic weight may have in producing the unsymmetrical action very reasonably to be expected at a junction, it cannot act quite in the manner suggested in § 29; for the difference between the out and in velocities of any particular substance must really depend only on its own physical properties, and not on those of the substance with which it is put into contact.

$$j\Pi u. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The roots of the equation $\Pi=0$ will give temperatures at which there is no electromotive force, or at which the two metals are neutral to one another. There are only two positive roots: $\theta=0$ is of course one; for then all molecules are standing still. The other will be the neutral temperature of Cumming; a first approximation to it is

$$\theta_0 \bumpeq \frac{-2\mathrm{A}(h'_a-h''_a)\log a+2\mathrm{B}(h'_b-h''_b)\log b}{\mathrm{A}(h'_a-h''_a)(\log a)^2-\mathrm{B}(h'_b-h''_b)(\log b)^2}. \qquad (25)$$

§ 35. Leave this for the present, and proceed to find the electromotive force generated at a junction of two parts of the same metal A at different temperatures θ_1 and θ_2—or rather the electromotive force generated in a certain length of A, in which the temperature is gradually falling from the value θ_1 at one end to the value θ_2 at the other. Consider a small element with temperature θ, resistance r, and out and in velocities of the molecules v, $v+dv$ at one end; and at the other, temperature $\theta+d\theta$, resistance $r+dr$, and velocities v_1 and v_1+dv_1: then the force exerted on the positive cord in this element is, just as in (21),

$$\Delta\mathrm{F}=r'dv-(r'+dr')dv_1,$$

or in the limit

$$d\mathrm{F}=dvdr', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21')$$

which

$$=\mathrm{A}\theta dr',$$

since dv is proportional to θ (§ 29).

Similarly, the force on the negative cord is

$$d\mathrm{F}'=\mathrm{A}\theta dr'';$$

so the balance of electromotive force in the element is

$$d\Theta=d\mathrm{F}-d\mathrm{F}'=\mathrm{A}\theta(dr'-dr''). \quad . \quad . \quad (26)$$

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[*] I find I have not used the symbol in quite its ordinary sense: Thomson calls Πu the heat absorbed, and $\mathrm{J}\Pi$ the electromotive force. I have preferred my notation, however, as the J occurs more naturally in a quantity of heat than it does in an electromotive force.

Now (4)

$$dr = h\frac{\theta a^{\theta}\log a - a^{\theta} + 1}{\theta^{2}}\,d\theta\,;$$

hence, integrating,

$$\Theta = \int_{\theta_2}^{\theta_1} d\Theta = \mathrm{A}(h' - h'')\left\{a^{\theta_1} - a^{\theta_2} - \int_{\theta_2}^{\theta_1}\frac{a^{\theta} - 1}{\theta}\,d\theta\right\}, \quad (27)$$

a force acting in the direction from hot to cold when $h' - h''$ is positive.

This, then, is the coefficient of Thomson's effect; or if a current of strength u be sent through the metal in opposition to the above force, the heat generated per second is (§ 28)

$$j\Theta u, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

which will show itself as a convection of heat by the current in one direction or the other, according as h' is greater or less than h''. Thus, if the current *generates* heat or "carries heat with it" in passing through the metal from hot to cold, the electromotive force Θ must be acting from cold to hot; and therefore the bite of the buttons on the negative cord must be greater than on the positive, or h'' must be greater than h'. This is the case in copper. But, on the other hand, if the current *absorbs* heat in passing from hot to cold, so that the heat appears to travel *against* the current (that is, if the "specific heat of vitreous electricity" be *negative*), then the electromotive force Θ must be acting *with* the current, or from hot to cold; that is, h' is greater than h'', and the *positive* cord is most acted on. This is the case in iron.

The quantity of heat carried down *small* unit difference of temperature in unit time by unit positive current (that is, by unit quantity of vitreous electricity), Thomson calls ("without theory, but by an obvious analogy") *the specific heat of vitreous electricity in the substance* A, and writes it σ_a; in other words, the reversible heat generated by forcing a current u against the force Θ from a point at a temperature θ to a point at a temperature $\theta + d\theta$ is

$$jud\Theta = -\sigma ud\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The value of σ in any substance is therefore (26)

$$\sigma_a = -jA\theta\frac{dr' - dr''}{d\theta} = -jA(h'_a - h''_a)\theta\,.\,\frac{d}{d\theta}\left(\frac{a^\theta - 1}{\theta}\right), \quad . \quad (30)$$

and similarly, of course, for σ_b. Hence (23) obviously follows Thomson's relation

$$\frac{d\left(\frac{\Pi}{\theta}\right)}{d\theta} + J\frac{\sigma_a - \sigma_b}{\theta} = 0. \quad . \quad . \quad . \quad . \quad [15]^*$$

§ 36. It is easy now to find the total electromotive force of a complete thermo-electric circuit—that is, the electromotive force acting in a ring made of two metals A and B, one of the junctions being at a temperature θ_1, the other at a temperature θ_2; for we have simply to add the difference of the two Peltier effects to the difference of the two Thomson effects, (23) and (27), and we get

$$E = \Pi_1 - \Theta_a - \Pi_2 + \Theta_b = A(h'_a - h''_a)\int_{\theta_2}^{\theta_1}\frac{a^\theta - 1}{\theta}\,d\theta$$
$$- B(h'_b - h''_b)\int_{\theta_2}^{\theta_1}\frac{b^\theta - 1}{\theta}\,d\theta, \quad . \quad . \quad . \quad (31)$$

which is evidently equal to

$$\int_{\theta_2}^{\theta_1}\frac{\Pi}{\theta}\,d\theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [17]$$

as Thomson has shown it must be.

It is evident also from the form of Π, viz.

$$\Pi_{AB} = P_A - P_B,$$

that

$$\Pi_{AB} + \Pi_{BC} + \Pi_{CD} + \ldots + \Pi_{YZ} + \Pi_{ZA} \equiv 0, \quad . \quad (32)$$

provided θ is the same for all—or that the electromotive force in a ring formed of any number of metals all at the same temperature is zero. The values found for the effects therefore satisfy all the conditions laid down for them.

§ 37. So far I have written down the results of our hypothesis without any approximation; but simpler and nearly accurate values will be obtained by expanding them all in series and taking the first term or two, or, what comes to the same thing, by using the first two terms only of the expression (5) for r. Thus, writing

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[*] The numbers in square brackets refer to Thomson's equations so numbered in his papers on "The Dynamical Theory of Heat. Part VI.—Thermo-electric Currents," reprinted from the Trans. R. S. Edin., in the Phil. Mag. for March, April, May, and June 1856.

$$r'_a \bumpeq \alpha_0 + \alpha\theta, \quad r''_a \bumpeq \alpha'_0 + \alpha'\theta, \quad r'_b \bumpeq \beta_0 + \beta\theta, \quad r''_b \bumpeq \beta'_0 + \beta'\theta,$$

we get at once from the hypothesis all the results in the form given to them by Tait, and experimentally verified by him for moderate ranges of temperature. The contact-force at a junction (22) becomes

$$\Pi \bumpeq \theta\{A(\alpha_0 - \alpha'_0) - B(\beta_0 - \beta'_0) + \theta[A(\alpha - \alpha') - B(\beta - \beta')]\}, \qquad (33)$$

which is of the form

$$X\theta - Y\theta^2;$$

and the neutral temperature of Cumming is

$$\theta_0 \bumpeq \frac{X}{Y} = -\frac{A(\alpha_0 - \alpha'_0) - B(\beta_0 - \beta'_0)}{A(\alpha - \alpha') - B(\beta - \beta')}. \quad . \quad . \quad (34)$$

We may write for (33)

$$\Pi \bumpeq Y\theta(\theta_0 - \theta), \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

which will be precisely Tait's form (see Maxwell, p. 306) provided $jY\theta$ comes out to be the difference of the specific heats of electricity in the two metals at the temperature θ.

To find Θ, one has from (26)

$$d\Theta_a \bumpeq A\theta(\alpha - \alpha')d\theta,$$

or

$$\Theta_a \bumpeq \tfrac{1}{2}A(\alpha - \alpha')(\theta_1^2 - \theta_2^2), \quad . \quad . \quad . \quad (36)$$

whence, from the definition of the specific heat (29),

$$\left.\begin{aligned} \sigma_a &\bumpeq -jA(\alpha - \alpha')\theta, \\ \text{similarly} \quad \sigma_b &\bumpeq -jB(\beta - \beta')\theta; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (37)$$

and therefore, (33), the condition in (35)

$$jY\theta \bumpeq \sigma_a - \sigma_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

is satisfied.

The total electromotive force in a thermo-electric circuit is obtained, either like (31) by finding $\Pi_1 - \Pi_2 - \Theta_a + \Theta_b$, or by forming the integral $\int_{\theta_2}^{\theta_1} \frac{\Pi}{\theta} d\theta$; and its value is

$$E \bumpeq Y(\theta_1 - \theta_2)\{\theta_0 - \tfrac{1}{2}(\theta_1 + \theta_2)\}. \quad . \quad . \quad (39)$$

The law was originally given nearly in this shape by Avenarius*; but he omitted the two Thomson effects, and consequently his formula was erroneous. The above form is that of Tait †, who has verified it for moderate ranges of temperature.

Tait also shows that if T_{ab} stand for the temperature θ_0 at which two metals A and B are neutral to one another, and if σ_a be equal to $k_a\theta$ (where k is a constant), then must

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* Pogg. *Ann.* vol. cxix. (1863).

† Proc. R. S. Edin. 1870-71.

$$(k_b-k_c)T_{bc}+(k_c-k_a)T_{ca}+(k_a-k_b)T_{ab}\equiv 0.$$

Now from (34) and (37)

$$(k_a-k_b)T_{ab}=A(\alpha_0-\alpha'_0)-B(\beta_0-\beta'_0), \quad . \quad . \quad (40)$$

and the cyclical sum of three, or of any number, of such terms evidently vanishes.

University College, London.

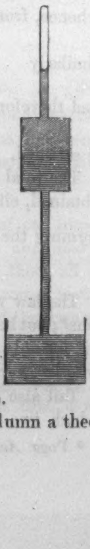
January 20, 1877.

XII. *A Sensitive Mercury Barometer.*

By Frederick Guthrie.

The object aimed at is to get a barometer which shall combine great sensibility with sufficient compactness. The barometers depending upon the weight of liquid columns are, unless the liquid is mercury, of unwieldy length. Descartes suggested a modification of the mercurial barometer in which the air-supported column of liquid consists of two liquids, the lower one being mercury and the upper one water holding tartar-emetic in solution to ensure the expulsion of air (fig. 1). Now that we know various liquids, notably hydrocarbons, which have no sensible vapour-tension at atmospheric temperatures, it is surprising that this form has not been reintroduced. It appears, however, to be little known. It was suggested to me by a friend; and I made one containing glycerine and used it with success for some months before I was aware of its having been suggested by Descartes. The sensibility of such a barometer would obviously be, if the upper liquid were without weight, directly proportional to the ratio between the sectional areas of the cylindrical chamber and the upper tube (if also the open limb were of infinite area). But, the upper liquid having weight, the limit of sensibility is the comparative density of the mercury and liquid (say 16 : 1). Accordingly this limit is reached when the cylindrical chamber has four times the diameter of the upper tube.

Fig. 1.

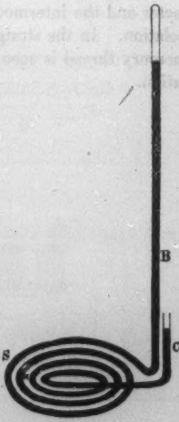


By inclining the top part of the supported column a theoretical increase of sensibility is obtained; but practically, on account of the dragging on the column and for other reasons, this device is not in use for exact measurements. The multiplication of motion caused by applying a float connected with a wheel, as in the common weather-glass, is for similar reasons to be discarded for such purposes. Aneroid barometers are of exceedingly convenient form, but are of course saddled with the objection that the metal chamber is never perfectly elastic, so that they require frequent comparison with standard mercurial ones.

My friend the late B. F. Duppa devised a barometer in which the cistern or open limb was dispensed with, and was replaced by an open horizontal capillary tube. The free surface of the mercury in the capillary tube would then move at a rate proportional to the sectional areas of the vacuum end and the capillary. I believe this plan was not found to answer, on account of the oxidation of the free end of the mercury.

The plan which I submit, and which in the models I have made and have had made appears to succeed well, more resembles that of M. Duppa than of any other with which I am acquainted. One form, shown in fig. 2, made for me by Messrs. Cetti, of Brooke Street, Holborn, consists of an ordinary barometer-tube, B, 6 millims. in internal diameter, connected by a flat horizontal spiral, S, of 2 millims. internal diameter, with the open tube C of the same diameter as B. In S is a bubble of air, *a*, at such a distance from B that it cannot enter B when the mercury in that tube is at the top. The motion of the bubble is, of course, 9 times as fast as that of the level of the mercury in either limb, or 4½ that of the true barometric variation. The object of bringing B and C together is to avoid as much as possible the effect of the relative differences of height on change of place. In another form (which is being made by Mr. Hicks, of Hatton Garden), the limb

Fig. 2.



C is made to enclose hermetically the limb B. This should bring the effect of such relative tilting to a minimum. In one which I have myself made, the tube S being straight and placed on a stone mantlepiece, a drop of sulphuric acid is employed instead of the air-bubble. It has the effect of making the motion rather more nimble, but is perhaps not quite so trustworthy for exact measurements, because the wetting of the tube by the liquid causes some inconstancy in its calibre. A tube S of 2 millims. internal diameter, connected with a barometer-tube having at its upper mercurial surface a diameter of 20 millims., would exaggerate barometric motion 100 times; and of course the sensibility would approach the nearer to twice this, the greater the diameter of the open limb. There is indeed absolutely no theoretical limit to the possible sensibility. It must be left to practical glass-workers to determine whether a spiral form is the best for the tube S, or whether a series of parallel tubes joined alternately end to end are to be preferred. According to Professor Dewar, who has had great experience in the use of such tubes for similar purposes, it would not be advisable to have the S tube less than 2 millims. internal diameter. In all cases, on account of the unavoidable irregularities in so long a tube, I presume as many as possible comparisons should be made with a standard barometer and the intermediate graduations introduced by interpolation. In the straight one mentioned above, the gap in the mercury thread is seen through a lens to be in constant agitation.

Fig. 1.

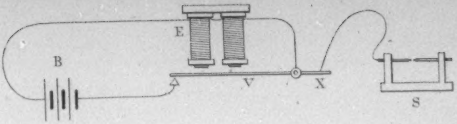


Fig. 2.

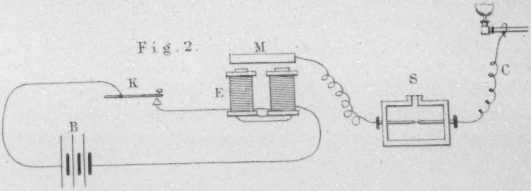


Fig. 3.

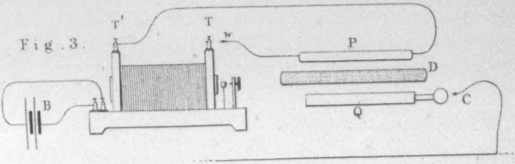


Fig. 4.

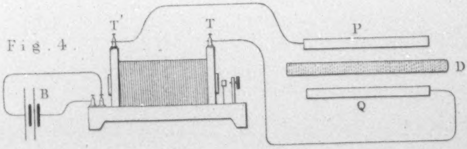
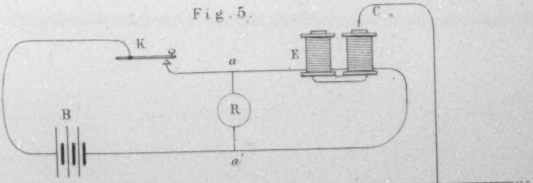


Fig. 5.



Mintern Bros. lith.

PROCEEDINGS
OF
THE PHYSICAL SOCIETY
OF LONDON.

MARCH 3, 1877.

XIII. *Note on the Polarization of Heat.*
By G. CAREY FOSTER, *F.R.S.*

THE following determinations of the amounts of heat transmitted by two Nicol's prisms, whose principal sections make different angles with each other, were recently made in the Physical Laboratory of University College, London, by Mr. M. J. Jackson. Although the results amount to nothing more than an additional verification of a relation that is already thoroughly established, I venture to put them on record, not only because such verifications are satisfactory in themselves, but also because the apparatus required for conveniently repeating experiments of this kind is not always at hand.

The source of heat was a rather powerful paraffin-oil lamp (supplied by White, of Glasgow, for use with a Thomson's quadrant electrometer). The rays from the lamp were concentrated by a lens of 7·5 centims. diameter and about 22 centims. focal length, placed so as to produce a real image of the lamp-flame within the silvered reflecting cone of the thermopile. Immediately behind the lens (on the side next the lamp) a double screen of polished sheet brass was placed, whereby the radiation could be cut off or allowed to pass at will. On the other side of the lens came two Nicol's prisms, each about 20 centims. long, and giving a clear circular field about 6·7 centims. in diameter. The prisms are protected at the ends by disks of thin glass, which were left on during the experiments. It is to the possession of these fine prisms, made for me by Mr. C. D. Ahrens, that the possibility of making the experiments with so much ease was due. The thermopile, which was about 95 centims. distant from the lens, was protected from stray radiation by a double hood of tin-plate. The galvanometer was a reflecting instrument of low resistance, on Sir William Thomson's principle, made by my assistant, Mr. Grant. By means of a commutator inserted between the thermopile and the galvanometer, two opposite deflections were obtained for each position of the prisms. In the following Table, the column headed δ_1 gives the means of the deflections to right and left when the angle, θ, between the principal sections of the prisms was measured in one direction; and the column headed δ_2, the corresponding deflections when this angle was measured in the opposite direction. The numbers denote divisions of the galvanometer-scale.

Angle between principal sections $=\theta$.	Deflections.			$\frac{\delta}{\cos^2\theta}$.	δ' (calculated).
	δ_1.	δ_2.	Mean δ.		
0°	32·25	31·5	31·9	31·9	31·1
15	29·75	29·25	29·5	31·6	29·0
30	22·75	23·5	23·1	30·8	23·3
45	14·75	14·75	14·75	29·5	15·5
60	7·75	7·75	7·75	31·0	7·8
75	2·25	2·0	2·1	31·7	2·1
90	0·5	0·25	0·4	......	0·0
			Mean ...	31·1	

The numbers in the last column of the Table are calculated by the formula $\delta'=31{\cdot}1\cos^2\theta$. It will be seen that the observed mean values (δ) never differ from the corresponding calculated values (δ') by a whole division of the scale, which represents about as high a degree of accuracy as can be expected from the method of observation employed, it being impossible to read with certainty to any thing less than half a division: where quarter divisions occur in the Table, they result from taking the means of positive and negative deflections.

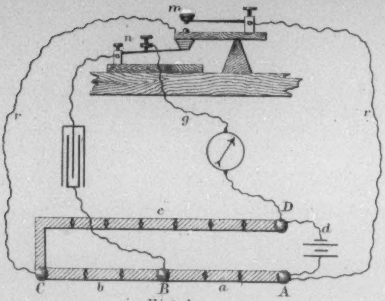

m
n
r
r
g
c
D
d
C
b
B
a
A

Fig. 1.

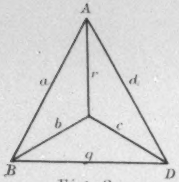


Fig. 2.

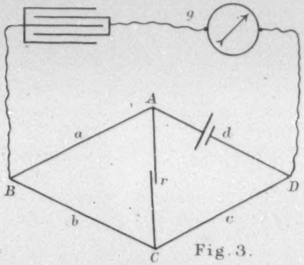

g
A
a
d
r
B
D
b
c
C

Fig. 3.

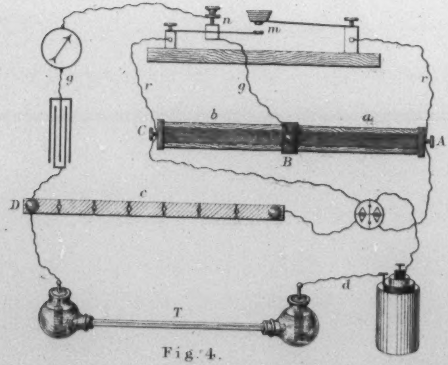

n
m
g
r
g
r
b
a
C
A
B
c
D
d
T

Fig. 4.

Mintern Bros lith.

XIV. *On a Modification of* Mance's *Method of measuring Battery Resistance.* *By* Oliver J. Lodge, *B.Sc.*

[Plate II.]

The modification here suggested consists simply in using a galvanometer and condenser instead of a galvanometer alone, so as to detect variations in difference of potential instead of variations in current.

By this change it is converted into a strictly *null* method. Moreover it is now possible entirely to get rid of the effects of variations in the electromotive force of the battery, which are very annoying in any of the ordinary methods and prevent accurate measure. This is accomplished by breaking the galvanometer-circuit the instant after the battery is short-circuited. Fig. 1 (Pl. II.) is a diagram of the connexions for measuring the resistance of the battery *d*, with the keys shown on a large scale: *m* partially short-circuits the battery when depressed; *n* closes the galvanometer and condenser circuit *unless* depressed. The two keys are electrically independent; but the stand of the upper one is balanced so as to rest partly on the spring of the lower one (which must be strong). On depressing the upper key, the first effect is to close the circuit marked *r* at the point *m*; the second, and immediately succeeding, effect is to break the circuit marked *g* at the point *n*. The same object would be accomplished more conveniently by a single double-contact key made on purpose, as shown in fig. 4. The object of the double key is fully explained below. A B C D represents a box of resistance-coils; *a* and *b* are large and equal resistances; and *c* will be equal to *d*, the resistance of the battery, whenever the galvanometer-needle is unaffected by pressing down the keys.

Resistance-measurements in general.

Consider the arrangement of six conductors joining four points (commonly known as the Wheatstone's bridge) as forming the edges of a tetrahedron or triangular pyramid (fig. 2). It is obvious, (1) that, as far as position is concerned, every conductor has precisely the same properties as any other, and (2) that any one conductor is adjacent to four of the others and opposite to the remaining one. Call the resistances of pairs of opposite ones a and c, b and d, r and g, and let electromotive forces be caused to act in any manner through any of them; then it can be shown that when $ac=bd$, r and g are "conjugate conductors," or that variations in the conductor r have no effect whatever on the current in g, and *vice versâ*, no matter whether these variations are simple changes of resistance or the introduction of new electromotive force.

By ascertaining, then, whether the insertion or removal of batteries at r has any effect on a galvanometer at g, one can observe whether the relation $ac=bd$ is or is not fulfilled, and can change one of these resistances until it is. For the case when a, b, c, and d are simple metallic conductors, this is Wheatstone's method of comparing their resistances.

Again, reciprocally, when this relation is fulfilled, no change in g can affect the current through the battery in r; and therefore, if this battery in r is the only electromotive force in action, a change in the resistance of g does not affect the current at all anywhere. Hence a galvanometer in, say, d will show a constant deflection whether the resistance of g is 0 or ∞, whenever $ac=bd$; and this is Thomson's method of measuring the resistance of the galvanometer d.

Further, from what has been said, there is no objection to an existence of electromotive force in any or all of the conductors, *provided it remains constant*; for it will be equally possible to observe whether changes in r (of any sort) have any effect on the current in g; and if not, then $ac=bd$, as before. For the case when d is a battery of constant electromotive force, this is Mance's method of determining its resistance.

But it must now be observed that although changes in r may have no effect on the current in g, they must affect very essentially the current every where else, and therefore through the battery d. This battery ought, then, to preserve its electromotive force constant in spite of variations taking place in the strength of its current—a thing which no known battery is capable of doing. The electromotive force of every battery is really a function of the current it is producing and of the time it has lasted. In cells called *constant* the dependence of electromotive force on current and time is only slight; but in none does it disappear.

This fact that the current* and consequently, to some extent, the electromotive force of the battery are made to vary by the process of measuring its resistance, constitutes a great apparent defect of the method; but it is an irremediable defect, and is not peculiar to this particular method. It is in fact *impossible* to measure the resistance of a battery without varying the strength of the current passing through it, by any method founded, as all our methods are, on a measurement of current or of difference of potential. In other words, just as it is impossible to measure any resistance whatever without the passage of a current through the resisting body, although it is quite easy to measure an electromotive force without any current circulating through the electromotor, so, although a current of constant strength is sufficient to give a measure of the resistance of a homogeneous conductor, such as a metallic wire of uniform material, or a homogeneous liquid, or any thing else which contains no internal electromotive force, yet a variable strength of current is necessary to determine the resistance of an electromotor.

And the reason of this is apparent, viz. that the opposition experienced by a current in passing through an electromotor is of two kinds—one due to the proper *ohmic* resistance, the other due to the electromotive force; and with only one strength of current it is no more possible to tell how much of the opposition is resistance and how much is electromotive force, than it is to obtain the values of two unknown quantities from one equation. We may either take two measures of the strength of current and then eliminate one of the unknown quantities algebraically, or we may use a contrivance (like Mance's method) by which one of them (viz. electromotive force) is eliminated electrically; but two strengths of current are just as essential in the latter case as in the former, as also it is just as necessary that the two unknown quantities shall remain constant. It is possible that the resistance, as well as the electromotive force, of a battery does not accurately fulfil this condition, but that it varies to some extent with the current;

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* Professor Clerk Maxwell, in describing this method ('Electricity and Magnetism,' i. p. 411), says that "the current in the battery is not in any way interfered with during the operation;" but this must be a mistake.

in so far as it does this, however, it is not a definite thing, and is incapable of accurate measurement.

I have entered into this matter at some length because the slip in Maxwell is getting repeated in other books (*cf.* Cumming's admirable 'Introduction to the Theory of Electricity,' p. 162); and it is as well to get clear on the subject.

The difference of potential required to force a current of strength C through an electromotor of resistance R and internal electromotive force ϵ is

$$E = RC \pm \epsilon.$$

Various methods may be applied to measure E and C; but no observation of a single value of E and C can determine R unless ϵ is known. Another observation with a different value of E and C must be made; and then ϵ can either be eliminated directly, or one can employ an indirect means of effecting its elimination, provided it remain constant. (If it does not remain constant, and if the law of its variation is unknown, no amount of experiments can eliminate it.) It is true that a single strength of current will suffice to determine R after ϵ is known; but in the determination of ϵ another and quite different strength of current (viz. zero) was employed.

A curious illustration of the impossibility of measuring the resistance of an electromotor by means of a constant current was noticed the other day in the physical laboratory at University College by Mr. H. F. Morley, who has found that the current produced by a certain form of gas-battery is, within very wide limits, almost independent of the resistance of its circuit. He endeavoured to measure the internal resistance of this battery by means of its own current, but found it quite impracticable.

Variation of the Electromotive Force of a Battery.

In what precise way the electromotive force of an ordinary cell depends on the current passing through it and on the time that current has lasted, I am not aware of any experiments which afford us information. But a law like the following seems not improbable.

$$E = Ae^{-\frac{pt}{R}} + B, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where t is the time the cell has been in action through the resistance R; so that the rate of change of E is proportional to the excess of the strength of current it is producing over the minimum strength to which it will ultimately fall, or

$$\frac{dE}{dt} = -p\frac{E-B}{R}: \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

p is a number which may be constant, or it may be a function of the current or of t; but for a cell making any pretensions to constancy, it must be small. A and B are constants such that $A+B$ is the initial and B, the final, value of E.

At any rate we may, I think, reasonably assume that E is not affected instantaneously, however much the resistance of the circuit R is changed, but that it takes a certain time to change its value appreciably; consequently, if we only change R for an instant of time and then restore it to its original value, E may be regarded as constant. It is this fact, I apprehend, which gives Mance's method its practical value, and renders it superior to the somewhat similar methods of Siemens and Thomson, because in it the change of resistance of r can be made very rapidly without disturbing the galvanometer, and need only last a few seconds. The shortest time, however, is sufficient for some variation to take place in the battery; and accordingly a kick of the needle is usually observed, like that produced by an extra current, which is very annoying. The modification which I have to propose, however, renders possible so great a virtual diminution of the period of contact that this disappears.

Modification of Mance's Method.

There is also a practical objection to the ordinary form of Mance's method, not relating to its essentials, but to its sensibility and convenience, which the modification is intended entirely to remove. It is this:—The galvanometer in g, whose function it is to indicate any change in the current in that branch, has always a certain current passing through it, and its needle is therefore deflected more or less, according to the sensibility of the galvanometer; but the current produced by an ordinary cell whose resistance one wishes to measure is usually such as one does not care to pass through a delicate instrument, even if the excessive deviation it produces be corrected by external magnets. A rough galvanometer is therefore generally employed, and the needle is brought back reasonably near its mean position by magnets placed near it. But the needle being thus constrained by immersion in a powerful magnetic field, is by no means under favourable conditions, and only comparatively large changes in the current can be indicated by it. To remedy this defect and to make the method a *null* one, my first idea was to use a differential galvanometer and to send through its second wire a current from an auxiliary battery equal and opposite to the current produced in its first wire by the cell whose resistance is being determined, so as really to neutralize instead of merely to overpower its action on the needle. Or, without using a differential galvanometer, we may balance the electromotive force in the galvanometer circuit by means of an auxiliary closed battery circuit after the manner of Poggendorff. If either of these arrangements be adopted, we can use a sensitive Thomson's galvanometer, and its needle may be as nearly astatic as we choose. But it is not easy to get the two batteries under such similar conditions that they shall constantly oppose one another exactly; and though these arrangements may be useful in some cases, they are rather complicated and the adjustments somewhat difficult to make.

The next alteration which suggested itself consisted in interposing a condenser in the galvanometer circuit (see fig. 3). This effectually prevents any continuous circulation of electricity in that branch; and the galvanometer therefore remains at zero after the condenser has acquired its full charge; but any variation in this charge is indicated by a throw of the galvanometer-needle proportional to the amount of variation. The quantity of electricity flowing into or out of the condenser through the galvanometer-coil will be equal to the variation of potential, Y, taking place between its terminals multiplied by S, its statical capacity; and the throw of the galvanometer-needle α will be proportional to this quantity multiplied by the galvanometer-constant Γ, which depends directly on the number of turns of wire on it. The resistance of the galvanometer is quite immaterial. If H is the strength of the magnetic field in which the needle hangs and T the time of a complete oscillation of the needle in that field, we have

$$\sin\frac{\alpha}{2}=\frac{\pi\Gamma SY}{HT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By using, therefore, a galvanometer with a very large number of turns, and a condenser of great capacity, one can increase the sensitiveness of the method to any extent.

The investigation of the distribution of currents throughout the circuit becomes very simple now that there is no continuous current through the branch g. The connexions are shown in fig. 3, where AC is the branch r, whose resistance can be changed at pleasure from infinity to something near zero. Let A, B, C, D, be the potentials of the four corners; let d be the resistance of the battery we wish to measure, ϵ its electromotive force, and u the strength of the current passing through it. We want the difference of potential $B-D$ to be wholly independent of the potentials of A and C, which will be altered by changing r. Now as there is no current through g, we have the same current passing through b as through a—that is,

$$\frac{A-B}{a}=\frac{B-C}{b}, \text{ or } B=\frac{Ab+Ca}{a+b};$$

similarly

$$D=\frac{(A-\epsilon)c+Cd}{c+d};$$

hence

$$B-D=\frac{(A-C)(bd-ac)+\epsilon c(a+b)}{(a+b)(c+d)}, \quad . \quad . \quad (4)$$

which shows that the difference of potentials between the terminals of the condenser is independent of the potentials A and C as soon as the condition $bd-ac=0$ is satisfied.

We may conveniently write the above expression in terms of the strength of the current u passing through the battery d; thus, since $A-C=\epsilon-(c+d)u$,

$$B-D=\frac{(ac-bd)u+\epsilon b}{a+b}. \quad . \quad . \quad . \quad . \quad (4a)$$

So, if $ac=bd$, the difference of potential $B-D$ is quite independent of the current through the cell (except in so far as the electromotive force ϵ depends upon it) and is equal to $\frac{\epsilon b}{a+b}$ or $\frac{\epsilon c}{c+d}$, which are the same thing.

The current u is of course dependent on the resistance r of the branch AC, being

$$u=\frac{(a+b+r)\epsilon}{(a+b)(c+d)+r(a+b+c+d)}; \quad . \quad . \quad . \quad (5)$$

so we may also write the above difference of potential in terms of this resistance r, thus :—

$$\mathrm{B}-\mathrm{D}=\epsilon\,.\,\frac{(a+b)c+r(b+c)}{(a+b)(c+d)+r(a+b+c+d)}. \quad . \quad . \quad (4\,b)$$

All the differential coefficients of this with respect to r contain the factor $ac-bd$; consequently when this factor vanishes this quantity is independent of r.

Conditions for Sensitiveness.

To find out what are the values of a, b, and c which give the greatest sensitiveness, we can subtract the value of B−D when r is infinite from its value when r is zero, and can make this quantity a maximum when the condition $ac=bd$ is nearly fulfilled. The quantity which has to be a maximum is

$$y=(\mathrm{B}-\mathrm{D})_0-(\mathrm{B}-\mathrm{D})_\infty=\frac{\epsilon(ac-bd)}{(c+d)(a+b+c+d)}. \quad . \quad . \quad (6)$$

The resistance d is supposed to be given; so let us define the others with reference to it, putting

$$c=\lambda d,\ a=\mu d,\ \text{and}\ b\bumpeq\lambda\mu d=\lambda\mu(1-z)d,$$

where z is a small quantity; then the above quantity becomes

$$y=\frac{\lambda\mu z\epsilon}{(\lambda+1)^2(\mu+1)}. \quad . \quad . \quad . \quad . \quad . \quad (6\,a)$$

Considered as a function of λ, this is a maximum when $\lambda=1$; it has in fact the same value whether $\lambda=n$ or $\frac{1}{n}$. Considered as a function of μ, it has no maximum, but it is greatest when μ is infinite, though it does not increase fast after μ is tolerably large; the curve is, in fact, a rectangular hyperbola with asymptotes $y=1$ and $\mu=-1$; and 1 is its greatest value for positive values of μ. Accordingly the most sensitive arrangement is obtained when $\lambda=1$ and when $\mu=\infty$—that is to say, when c is equal to d (the resistance to be measured), and when a and b are equal and as large as convenient. When these arrangements are made, the maximum value of y, or the change in the difference of potential between the terminals of the condenser brought about by depressing the key, is, when c is nearly equal to d,

$$\mathrm{Y}=\tfrac{1}{4}\epsilon z \quad \text{or} =\frac{\epsilon}{4}.\frac{c-d}{d}; \quad . \quad . \quad . \quad . \quad (7)$$

and this is the quantity to be inserted in equation (3).

The sensitiveness is evidently directly proportional to the electromotive force of the cell: but it is independent of its resistance; *i. e.* a high resistance is measured with as great proportional accuracy as a low one. But it must be remembered that when the resistance to be measured is great, the resistances a and b should be as great also; if they are not as great as d, the sensitiveness falls off very appreciably. But, as said before, there is really no limit to the sensitiveness of the method; for the size of the condenser and the length of wire on the galvanometer may be increased to any extent.

Practical Details.

The condenser I have used is a small standard one with the dielectric of mica; and it has a capacity of slightly over one micro-farad. The galvanometer is a Thomson astatic by Elliott, with a resistance of about 7000 ohms. The two branches a and b of the resistance-coils, forming the equal arms of the bridge, were 1000 ohms each, being the largest resistance conveniently available in the box of resistance-coils used. But when the resistance to be measured is large (say over 500 ohms) it is better to have a and b greater than this; and they may then be made of Muirhead's carbon-paper (fig. 4). A strip 2 feet long by half an inch broad will have a resistance of about 14000 ohms; and the galvanometer terminal B may be connected with its middle so as to divide it into two halves representing a and b. Exact equality in the two arms is not essential, as it is easy (and, indeed, generally advisable) to eliminate any errors of this sort by a method analogous to double weighing. Connect a and b to a commutator in such a way that it is easy to interchange them end for end (see fig. 4), and balance the resistance d by the coils c; then interchange a and b and balance again; this time we may require an amount c'. Then it is easy to see that $d=\sqrt{(cc')}$, whatever the ratio of a to b; for in the first case we have $d:c=a:b$, and in the second $d:c'=b:a$. If c and c' are nearly equal, their arithmetic mean may be taken instead of their geometric, as being easier to calculate.

Use of a Double-wire Galvanometer as an Electrometer.

When a differential galvanometer, or a galvanometer with two long fine wires wound side by side, is employed, a separate condenser is not absolutely necessary; for the galvanometer itself has a certain capacity, and in order to charge one of its wires up to the potential B, and the other down to the potential D, a certain quantity of electricity must flow into the one wire and out of the other, and any variation in this quantity will affect the needle (though the galvanometer-constant has only half its ordinary value). Even when a separate condenser is used the capacity of the differential galvanometer may be taken advantage of, by connecting the terminals of the condenser to its two middle screws (instead of joining them directly to each other by a wire and inserting the condenser as in fig. 3), so that both condenser and galvanometer get charged instead of only the condenser. The defect of this method is, that the insulation between two silk-covered wires is not very perfect, and there is a slight leakage, which maintains a slight continuous deflection of the needle when the two outer screws are joined up to a battery; moreover the statical capacity of an ordinary fine-wire differential galvanometer is not very great.

But I think it may be often convenient to use a double-wire galvanometer as an electromoter in this way. For instance, rapidly to compare the electromotive force of any number of cells, join them up to the outer screws of the galvanometer with disconnected wires one after the other; the kick in each case measures the electromotive force of the cell. It might also be used to measure very high resistances. It is quite possible, and indeed very probable, that this method has been suggested before.

Elimination of Variations in Electromotive Force.

It has been stated above that if only momentary variations are made in the resistance r, or in the value of u, we can consider ϵ, the electromotive force of the battery, constant. The plan I adopt is to make the *effective* variation of r, or the variation which is to have any influence on the galvanometer, very short indeed. And this is done by arranging that the key m which closes the circuit of r shall break the galvanometer circuit g, the instant after, at the point n, as shown in figs. 1 and 4. For an instant, then, u is varied; and if the resistances are not balanced so that $ac=bd$, a certain quantity of electricity will enter or leave the condenser through the galvanometer; but variations in ϵ (due to the changed u), which would produce the same effect on the galvanometer, no matter how much the resistances were balanced, have no time to take place before the galvanometer circuit is broken; and then no further change has any effect. This works very well in practice; and the resistance of a cell can be really determined when producing a current through a definite resistance, viz. $a+b+c+d$. This cannot be done accurately by any other method that I know of.

Measurement of any Liquid Resistances.

The method may be applied to determine the resistance of electrolytes in general. A long tube containing the electrolyte surrounded by a jacket of water at a known temperature is interposed in the battery circuit d, the battery being one whose resistance is small and can be depended on; and the resistance of the two together, battery and tube, is measured.

The tube is then removed, and the resistance of the battery determined alone; the difference of course gives the resistance of the electrolyte in the tube. The tube can then be filled with mercury and the measurement repeated. The amount of polarization of the electrodes is of no more consequence than the electromotive force of the battery, provided the gas given off is not allowed mechanically to obstruct the current; and the effect of variations in its amount are reduced to a minimum by the method just described for the battery. It is well to make the tube end in a couple of globular receivers with two necks, very much like Dewar's electrometer, and to plunge large electrodes into these globes (see T, fig. 4). Their position in the globes is not of very much consequence; neither is a bubble or two of gas on their surface; the principal part of the resistance is offered by the liquid in the tube. If a thermometer is kept in each receiver and the liquid be allowed to flow backwards and forwards through the tube once or twice before observing, its temperature may be known without surrounding it with a jacket. But of course this does not apply accurately when it is required to raise its temperature much above that of the atmosphere. Since the sensitiveness depends on the electromotive force of the battery, it is well to use one or two Grove's cells. Fig. 4 is a complete diagram of the connexions, showing the arrangement for interchanging *a* and *b* by means of a commutator, and also showing a key which will break the galvanometer circuit at the instant required and act instead of the extemporized arrangement of two keys depicted in fig. 1. The lower spring carries a block which presses up against a screw connected with the galvanometer, except when it is forced down by the upper spring. This block is insulated from the spring, which carries it, but is connected with the point B. The interval elapsing between the breaking contact at *m* and the making at *n* is, and must be, utterly inappreciable. For the shortest practicable interval is sufficient to allow the currents to adjust themselves, unless *a* and *b* are extravagantly large resistances; and if it is not exceedingly short, disturbances will occur due to variations in the battery.

The diagrams purposely show the galvanometer, and not the condenser, connected with the breaking-key *n*, because leakage of the condenser is sure to occur to some extent when its circuit is broken, and, in order that this may not in the least signify, one terminal of the galvanometer must be insulated.

University College, London.

May 12, 1877.

XV. *On the Chromatic Aberration of the Eye in relation to the Perception of Distance.* *By* SILVANUS P. THOMPSON, *B.A.*, *B.Sc.*

1. THE experimental researches of Wollaston, Arago, Fraunhofer, Young, Matthiesen, Brewster, Müller, and Helmholtz have left no doubt that the eye has the defect of chromatic aberration. Rays of light of dissimilar colour, starting in the same direction from any luminous point and entering the eye, do not all come to focus upon the retina at once, but the foci for differently coloured rays are differently situated with respect to the retina.

Hence, so far as the perception of the distance of a luminous object is dependent upon the accurate focusing of rays upon the retina of the eye, so far the want of adjustment in the eye introduces a source of error into the data of our perception. If the eye be not achromatic, a blue object and a red object of equal dimensions placed side by side cannot be in focus at once, and hence must appear either unequally distant or else of unequal magnitude.

2. The object of this paper is to demonstrate that the fact thus briefly sketched out affords a true and legitimate explanation of certain empirical rules of artistic practice relative to the pictorial expression of distance. The existence and universal recognition of such empirical rules has presented itself as a problem to the mind of the writer for the past six years; but it is only within the last few months that the solution now offered has been adopted by him.

It is proposed therefore :—

I. To enumerate the various data dependent on the eye and not upon the feet or other limbs, for the formation of a perception of distance.

II. To discuss the weight to be attached to the several data under various circumstances.

III. To inquire how far these data may be dependent upon the apparent colour of an object, or upon the formation of an exact focus upon the retina of the eye.

IV. To give a brief account of some experimental results, together with conclusions derived therefrom.

I. *Data for the Perception of Distance.*

3. The following nine data may be enumerated as contributing to the formation of a perception of distance.

4 (*a*). Apparent motion of objects caused by motion of the observer. If we move from one place to another, or alter the position of the head, the visible configuration of objects suffers a corresponding change, which by association with previous experience suggests an external system, of whose distance this "parallax" affords us an idea.

5 (*b*). Apparent change of configuration of objects according as they are viewed with one eye or the other. This affords a "parallax" similarly to (*a*), though on a more limited scale.

6 (*c*). The muscular sensation of convergence or divergence of the two eyes when directed towards an object. This is a genuine muscular perception, though guided by the optical perception of want of positional adjustment when the corresponding parts of the two images do not fall upon the corresponding points of the two retinæ.

7 (*d*). Retinal magnitude of an object as appreciated by the muscular effort of turning the eyeball so as to bring the parts of the image successively into the centre of the field of vision.

8 (*e*). Retinal magnitude as a sensation of excitement of a certain area of nerve matter of the retina.

9 (*f*). The muscular sensation of effort of the ciliary muscle in the adjustment of the eye to exact focus. The perception of exactness or inexactness of focus which guides the muscular action is, too, an optical effect in itself of little value as a means of estimating distance, except in so far as it controls the required muscular contraction.

10 (*g*). Binocular dissimilarity of the images on the two retinæ, which, conspiring to give one mental impression, present slight differences that suggest the idea of distance.

11 (*h*). Linear perspective. Under this term I propose to include, beside the usually understood play of lines and diminishing apparent magnitudes commonly spoken of as

perspective, such artificial means of estimating distance as are afforded by comparison with objects of known size (figures, cattle, &c.), and such notions of position, surface, &c. as can be drawn from comparison with houses or other objects of known form and magnitude.

12. (*i*) *Aerial Perspective*, in its widest sense. On this point Helmholtz has most aptly remarked* that the brain has the same means for the appreciation of relative distance as are employed by the painter on his canvas; and he enumerates amongst these means strong shadows, bold relief in the foreground, obscurity of atmosphere, and dimness of outline, in addition to contrasts with objects of known size or form. The term, however, is often restricted to the peculiar alteration of the colour of objects due to the intervening atmosphere†.

II. *Relative Importance of foregoing Data.*

13. It is obvious that the considerations advanced in (*a*), (*b*), and (*c*) are foreign to the present inquiry, though of enormous importance in the estimation of distances in general; for there can be no doubt that where these means are available, the mind is guided to a large extent by them in the formation of an estimate of distance, unless carefully trained to disregard them and to depend on other circumstances, or unless, as may happen to individuals, some physical injury has occurred to render the eye abnormal. With respect to the consideration advanced in (*c*), I have some reason to doubt whether we really do judge apparent distance by the muscular sensations of the external and internal recti muscles of the eye. Stereoscopic pictures appear to me equally "solid" whether in a Wheatstone's reflecting stereoscope, a Brewster's lenticular with prism-shaped lenses, or a Helmholtz's with parallel axes, or by superimposition by effort of the recti muscles, in each of which cases a different convergence is

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* 'Popular Lectures,' English edition, p. 281.

† Mr. Ruskin's definition of aerial perspective is, from an artistic point of view, of value. "Aerial perspective is the expression of space by any means whatsoever, sharpness of edge, vividness of colour, &c. assisted by greater pitch of shadow, and requires only that objects should be detached from each other by degrees of intensity in *proportion* to their distance."—'Modern Painters,' vol. i. p. 139.

required. Moreover it would be very inconvenient if our estimate of distance depended on the action of these muscles, as they are peculiarly liable to fatigue.

14. Retinal magnitude, to use the term adopted by Wheatstone, whether regarded in its muscular (*d*) or its optical (*e*) sense, affords only an indirect means of estimating distance by association with ideas previously acquired concerning the retinal dimensions of objects of known size at known distances. Nothing is more easy than deception arising from this cause. We constantly hear the magnification of the telescope spoken of as though the enlargement of the retinal image produced the same effect as if the object were brought so near to the eye as to yield a retinal image of equal area. This is evidently not the case, as the distant object, however much magnified in the telescopic image, is still seen by rays travelling in paths nearly parallel to each other, and not containing angles as great as those contained by rays proceeding from an object really near. Hence a telescopic presentation of an object is flatter than the object itself appears when brought sufficiently near to give a retinal image of equal magnitude.

15. The fallacy of judging distances by apparent magnitude is made evident by the absurd comparisons often made between the sun or moon and other objects, some individuals comparing them to the size of a coin, a plate, or a cart-wheel. Comparatively few persons could at once tell you correctly which appears the larger, the setting sun or a threepenny-piece held at arm's length—the fact being that the angular magnitude of the latter exceeds that of the former.

16. The following experiment * illustrates a remarkable power of accommodation of the eye to the requirements of the mind in respect of retinal magnitude. Place under a stereoscope a penny and a halfpenny, having the "heads" of both coins placed upwards and similarly. You shall see but *one* coin when looking with the two eyes, especially if you expect no dissimilarity and do not use the eyes alternately. There are, on the other hand, experiments of Helmholtz, Fechner,

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* My attention was first drawn to this curious fact by Mr. Joseph Beck, of the eminent firm of Smith and Beck.

and Volkmann[*] which go to prove that the retinal magnitude, as appreciated by the muscular sweep of the eye, affords a fairly accurate means of comparison of the angular magnitudes and positions of two objects in the field of vision whose images can be successively brought upon the same spot of the retina. This involves, however, the question of the persistence of visual impressions, without which such a comparison of retinal magnitudes might be quite fallacious.

17. The sensation (*f*) of tension of the ciliary muscle is a very delicate means of estimating near distances, and is a sensation capable of training to a considerable nicety. In October 1870 the writer was unable to perceive any difference of strain of adjustment to vision between distances of 4 yards and 400 yards. At the present time he is conscious of a difference of tension when the eye is directed to objects 15 yards and 300 yards distant respectively, and this with either eye. I insist on this means of estimation of distance, because it is, for monocular vision, of even more importance than the muscular sensation of convergence of the optic axes is for binocular vision.

18. The researches of Wheatstone, Brewster, Dove, Helmholtz, Brücke, Müller, Rood, Volkmann, and Wundt upon the stereoscopic presentation of objects resulting from the binocular dissimilarity of the two retinal images (*g*) illustrate the importance of this fact of binocular vision. Wheatstone's pseudoscope proved the point by a *reductio ad absurdum*; and an equally conclusive proof is obtained by cutting a stereoscopic slide in two and placing the halves in laterally reversed position under the stereoscope. I have, however, experimentally found that considerations of colour may sometimes outweigh the judgment founded by the eye upon the element of dissimilarity. I drew a pattern of two squares of four blue lines each upon paper, and within each, and outside each, centrally described circles in red. When this pattern was viewed in the stereoscope, the blue squares seemed to draw back from the eye. I then traced some of Möser's crystal forms from the well-known lithographed stereoscopic slides, colouring the *front* lines of the crystals with ultramarine, and the *back* lines

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[*] Helmholtz, 'Popular Lectures,' p. 279; and *Physiologische Optik*, pp. 522–524 and 542.

with vermilion. Several, though not all, of these when placed in the stereoscope refused to appear of their true form, the blue lines, whose positions would stereographically give a front presentment, retiring behind the red lines of the crystal.

That the mind does, however, habitually make use of the dissimilarity of binocular vision is evident from the old trick of looking with one eye through a short tube while attempting to walk up to a suspended ribbon and cut it with a pair of scissors. Yet persons who have the use of but one eye find no difficulty in performing the task; and, with practice, the feat becomes easy if the distance be carefully estimated by the sensations of ocular focus. The linear distance between the two eyes, however, sets a limit to the range of habitual estimates of distance founded on the fact of binocular dissimilarity; and, as Mr. Ruskin has observed *, it is possible to see, and to see in focus together, the extreme distance and the middle distance of a landscape, though the foreground and distance cannot so be seen together.

19. I cannot here dwell upon questions involving linear perspective (*h*). The various considerations upon which linear perspective becomes a basis for the perception of distance are purely associative—mental rather than optical, geometrical rather than physical.

20. I pass on, therefore, to aerial perspective (*i*); the various definitions of which may be summed up in one as the expression of distance by colour. A distant hill looks bluer than a less distant one by reason of the slight opacity of the intervening atmosphere ("sky"); and its blueness is in some manner, to a normal eye, a far truer measure of its distance than any one of the considerations yet treated of. The blueness thus existing in nature varies with the changing conditions of atmosphere, and hence is liable to be fallacious when the atmo-

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* Mr. Ruskin advances this point in defence of the practice of landscape-painters in leaving foregrounds sketchy and unfinished, maintaining that they should exhibit "a decisive imperfection, a firm but partial assertion of form which the eye feels indeed to be close home to it, and yet cannot rest upon, nor cling to, nor entirely understand, and from which it is driven away of necessity, to those parts of distance on which it is intended to repose."—'Modern Painters,' vol. i. pp. 183 and 184, note. Mr. Ruskin adds that Turner was the first to introduce this treatment into landscape art.

spheric conditions are unfamiliar. Thus in Smith's 'Optics' it is narrated of Bishop Berkeley that, when travelling in Italy and Sicily, he thought the cities as he approached them two or three miles too near, by reason of the unfamiliar transparency of the air.

III. *Bearing of Chromatic Aberration upon the foregoing Data.*

21. Taking the chromatic aberration of the eye as an established matter *, it is now time to inquire how far these various considerations are affected by the fact that rays of different colours have different focal length in the eye.

22. Obviously all estimates of distance which depend on retinal magnitude are liable to be influenced by colour. This may easily be verified by taking two equal disks of red and blue paper and placing them upon a black background. It will be found impossible to get a perfectly distinct image of both at once, one or other being out of focus, and therefore blurred at the edge and larger; or if no difference in size appears, one (the blue one) will appear more distant. The experiment may be varied by giving various sizes and shapes to the coloured disks, but with the same result, especially if the disks be looked at with one eye only. Orange and green disks may answer the purpose, but not so well as disks of red and blue, as these colours are most widely separated on the spectrum†.

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[*] In 1835 Brewster wrote: "I consider the *non-achromatism of the eye* as a fact as well established as any other fact in natural philosophy," Phil. Mag. 1835, p. 161.

[†] Brewster called attention to similar phenomena produced by coloured outlines in 'Brit.-Assoc. Report,' 1848, p. 48, "On the Vision of Distance as given by Colour." He there gives a rather laboured explanation, comparing the vision of different distances for the differently coloured lines to the phenomena of the lenticular stereoscope. He adds that "the difference of distance of the coloured lines or spaces may be appreciated even with one eye." Compare also Helmholtz, *Physiologische Optik*, p. 645.

Compare also an experiment with a disk of black paper on a background of pale ultramarine, by Prof. O. N. Rood, 'Silliman's Journ.' xxxi. 1861, pp. 343, 344.

There is little doubt that Wheatstone's phenomenon of the "Fluttering Hearts" (see 'Brit.-Assoc. Rep.' 1844) is due to the attempt of the eye to focus for adjacent spaces of colours of unequal refrangibility, which

23. On this account I am disposed to think that retinal magnitude has little to do with the appreciation of distance, except in the case of objects whose magnitude and tint are familiar to us ; and I shall show other reasons for the opinion. Hence I regard as very imperfectly true the statement of the late Sir Charles Wheatstone, in the Bakerian Lecture for 1852 *, that "Convergence of the optic axes therefore suggests fixed distance to the mind; variation of retinal magnitude suggests change of distance." I think that the muscular sensation of convergence of the eyeballs serves rather to give an idea of rate of change of distance †; and I have just indicated the cases to which variation of retinal magnitude are limited.

24. In Wheatstone's classical research of 1838 it was demonstrated how great is the capacity of the brain to combine together two slightly differing retinal images. This faculty once admitted, however explained, renders it unnecessary here to discuss how far the inexactness of focus for any particular tint is concerned in binocular vision. In the present paper it must suffice to treat of the non-achromatism of the eye in its relation chiefly to monocular vision. And, for reasons stated in § 19, we shall omit further reference to linear perspective, since its relation to our perception of distance is not based upon apparent colour, or upon the formation of an exact retinal focus.

IV. *Experimental Results, and Deductions.*

25. Fraunhofer ‡ is generally credited with the first careful attempt to measure the chromatic aberration of the eye. His method of experiment consisted in placing a wire in the principal focus of a telescope, in which the focus was then obtained by the adjustment of the lenses of an achromatic eyepiece. The theoretical adjustment to distinct vision for the

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could not, therefore, be in distinct focus at one time. The same peculiar fluttering is observed when white objects on a dark ground are observed through a purple solution of permanganate of potash.

* Phil. Trans. 1852, p. 4.

† See a curious little footnote by Mr. A. J. Ellis at p. 97 of his edition of Helmholtz's 'Sensations of Tone.'

‡ See Gilbert s *Annalen*, lvi. 1814, p. 304; Helmholtz, *Physiol. Optik*, p. 128; Brewster, 'Edin. Phil. Journ,' xix. p. 25.

various coloured rays was then calculated and compared with the actual adjustment; and the difference between theory and observation was assumed to measure the aberration of the eye. The method is at best only indirect; and there appears to be some doubt whether in the critical experiments an achromatic object-glass as well as an achromatic eyepiece was employed. Nevertheless, under the conditions of the experiment, the measurements were very accurately made, and are therefore invaluable.

26. I have found the most satisfactory exhibition of chromatic aberration to be manifested when a solution of permanganate of potash was employed, in a narrow glass trough, as a medium to intercept the middle rays of the spectrum. I have also tried solutions of iodine, and cobalt glasses of various depths of tint; but none are so satisfactory. For some experiments I have employed a piece of thin cobalt glass in conjunction with a solution of permanganate. By this means I have obtained media transmitting red and blue-violet rays freely, but totally opaque to all rays between D and E, and nearly opaque to rays from C to D in the orange, and from E to F in the green and blue.

27. A silvered bead placed in the sunlight, and viewed through such a medium can by no possibility be seen with accurate focus for all rays. It appears either as a near red point of light surrounded by a blue haze, or as a distant blue light surrounded by a red haze *. The point of light seems to change distance from far to near, or from near to far, with the effort of the eye. This effect, however, is only to be well observed when the intensities of the red and blue rays are about equal; for if either predominate, the eye will focus for the brighter unless special care is taken to adjust and keep the required focus.

28. The researches of Jurin, Schreiner, Müller, Powell, and Trouessart have tended in favour of the view that the eye is achromatic at least for objects at the centre of the field of vision, when distinctly in focus. The fundamental illustration of this view is as follows:—Take any visible white object—say

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* This effect may be shown objectively to an entire audience by casting beams of light from a lamp through such a purple medium upon a silvered ball.

a square inch of white paper upon a black background. If the eye be focused for a distance beyond the white surface, it will appear blurred at the edges, being tinged outwardly with orange-yellow, inwardly with blue. But if the eye be focused for a point nearer than the white surface, it will appear tinged outwardly with blue, inwardly with orange-yellow, while at exact focus these bordering tints disappear. To explain this seeming achromatism of the eye it was argued by Wollaston, Young, Müller, and Matthiesen that the rays passed almost without refraction along the axis of the eye, and therefore suffered no dispersion *. On the other hand, in my own experiments with permanganate-of-potash solution to intercept the yellow and green rays, I have never been able to obtain a luminous surface small enough to be free from aberration at the edges—which proves that the focus is really not exact. The rays of the middle of the spectrum, being more intense, mask the effects of the feebler rays; and the eye focuses for the more intense light, as I have mentioned in § 27.

29. If, on the contrary, a weak solution of picrate of potash be employed as a screen to cut off the extreme red and violet rays, it is very difficult with *any focus* to observe the tinted margins.

30. Moreover the apparent achromatism of the experiment above mentioned is only found with pencils nearly coincident with the axis of the eye. Oblique pencils always give tinted margins in white light. This may be verified by looking at a set of concentric circles in white and black. If the eye be steadily focused for the white centre, no colours are seen at its margin, but may be observed at the inner and outer edges of the other circles. I have always found it possible to get yellow exterior margins to a white object at any distance; that is, I have always found it possible to focus for a further distance; but not *vice versâ*.

31. If a square of white paper be carefully tinted around the edge with blue, and laid on a black ground, it appears

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* Baden Powell contended that the refraction and dispersion of the vitreous humour being in the opposite sense to that of the crystalline lens, aqueous humour, and cornea, compensated the dispersion for axial pencils.

further off than a perfectly white square of the same size beside it, since the blue margin helps to correct the yellow rays that surround the image at a longer focus. In short, a blue-edged square appears like a white square looked at with too near a focus. The opposite effect is observed with a margin tinted yellow.

32. I adjusted a lenticular stereoscope to easy focus, then placed in it a sheet of white paper having two equal circles 1 centim. in diameter, described upon it at the appropriate distance—one red, the other blue. The joint effect of these two gave, apparently, a combination of a red circle with a slightly larger one of blue. On drawing a slightly smaller circle of blue, with the circle of red as before, they appeared to give exact coincidence.

33. Knowing the power of the eye to reconcile retinal images in magnitude (see § 16), I placed in the stereoscope a penny coloured blue and a halfpenny coloured red. They refused to be seen as one object. On replacing them by a red penny and a blue halfpenny, coincidence was, with some difficulty, obtained.

34. My next experiments attempted the direct estimation of the distance of objects by the focus of the eye apart from other means of estimation. A conical tube of metal, blackened interiorly, was taken, through which only a limited field of view was possible, the eye being placed at the smaller aperture. In front of this tube a screen of blackened cardboard was placed, capable of adjustment to any distance from 10 centims. to 350 centims. from the tube, and covered the entire field of view. Coloured glasses could be introduced in front of the tube. The objects displayed upon the cardboard screen in the centre of the field of vision were irregularly shaped pieces of white paper. These were cut by an assistant and adjusted—their distance and size being unknown to the observer, and varied between each experiment. Hence, under the conditions given, the eye could form no judgment of distance based upon apparent magnitude, upon parallax, or upon apparent form or shadow ; the estimation depended solely upon the muscular sensation of adjustment to focus. After a little practice this became moderately easy with white light, and the estimations were fairly within limits. With a screen

of yellow glass interposed no difference was experienced. When a ruby-red glass was employed, however, the estimations were generally, though not invariably, too small, and with a cobalt-blue glass generally (though not invariably) too great. The following is the mean of six experiments taken at random from a number made with a red glass, and of another six from those made with a blue glass.

	Red.	Blue.
Mean real distance	208 centims.	178 centims.
Mean estimated distance	163·1 ,,	199 ,,

35. When a solution of permanganate was employed in conjunction with a blue glass, giving equal intensities of red and blue rays, the attempt to estimate the distance of the white pieces of paper became perplexing in the extreme. The object seemed to be moving backwards and forwards as the focus changed from red to blue and blue to red.

36. After about forty experiments with blue and red glasses, the errors became less. Evidently the effect of practice was to sophisticate the result, the mind knowing the probable result beforehand, and making allowance involuntarily. The forty experiments were not all made at one time, because the eye becomes fatigued when experimentation is prolonged; and as in my own case with fatigue partial astigmatism sets in, I was careful to test my vision from time to time, to avoid error from this source *.

37. Every book on Art will tell us that blue is a "retiring" colour, while red is an "advancing colour." For long I had been convinced that these alleged characteristics were something more than associations with blue sky and red rocks; and the universality and tenacity with which artists pronounce

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* Since the experimental results recounted in this paper have been chiefly obtained with my own eyes, it may be well to state the following particulars:—For objects in centre of field of vision there is no trace of colour-blindness; neither eye is astigmatic when not fatigued; their range of accommodation is from 11 centims. to infinity, and with good definition at all ranges; the blind-spots are distinct, the foveæ centrales well formed and sensitive; there is no difficulty in perceiving Purkinje's figures and Haidinger's brushes and lavender streaks. Let me add, as a test of definition, that on a clear night I can easily see twelve stars of the Pleiades.

this opinion is surely indicative of a reality somewhere. The opinion of Goethe on this point sums up the whole matter. I quote from Sir Chas. Eastlake's edition of the 'Farbenlehre'*.

"As the upper sky and distant mountains appear blue, so a blue surface seems to retire from us."

"Rooms which are hung with pure blue appear in some degree larger, but at the same time empty and cold."

38. So the blueness of the lower misty air may, as Alpine travellers know, cause the base of a mountain actually to appear *more distant* than its summit. Mr. Ruskin has noted this in his 'Modern Painters'†; and the fact has been familiar to artists for centuries, having been described by Leonardo Da Vinci in his *Trattato della Pittura*, and is alluded to by Goethe.

39. The sun and moon when red at setting or rising, and the moon when red in total eclipse, look nearer—or, some people say, larger—than at other times.

40. For the sake of giving prominence or nearness to the foreground of a picture, painters will contrive to introduce a scarlet flower, or a patch of red rock, or a figure dressed in red—a practice sanctioned and well known in Art, but quite inexplicable except on the train of reasoning we have been attempting to follow.

41. The immense importance of these facts of physical and physiological optics has long been recognized in Art. The study of aerial perspective has been carried long since to a pitch that renders it worthy to be put upon a basis more than merely empirical. There can be little doubt that other empirical laws may be similarly accounted for. Visitors to picture-galleries may be constantly observed scanning a landscape through a rolled up catalogue, or under the arched fingers of the hand. Is there not an explanation, too, for this? The square frame of gold asserts the flatness of the surface, and prevents the mind from realizing that which the eye perceives—that all the rays of light do not focus at once upon the retina, but that each tint retires or advances to its

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* Goethe's 'Theory of Colours,' translated by Sir C. L. Eastlake, R.A., F.R.S. (London: 1840), p. 311, par. 780 and 783.

† Vol. i. p. 182.

own appropriate distance. Landscapes without figures or architecture, especially, are improved by this method of treatment; and the reason is plain: in them the eye judges the scene by colour, not by retinal magnitudes or binocularly compound sensations.

42. I have endeavoured to apply the method of experimentation in another direction. Take any picture in which there are well-expressed foregrounds and distances, and look at it through the coloured media employed in the earlier experiments. If the facts of distance are expressed only indirectly, by suggestions of magnitude, by linear perspective of vanishing lines and the like, the interposition of a red or a blue glass will produce little effect, except that the latter may deaden the intensity of the shadows. If, however, the expression of distance in the picture is accomplished chiefly by aerial perspective (that is to say, by colour), a red glass will almost destroy the intelligibility of the picture, while a blue glass will draw out the distances in a marked manner.

43. Reflecting how useful is the purpose subserved thus by the non-achromatism of the eye, I consider it probable that if the eye were so constructed as to be originally achromatic, having usually blue distances and red-brown foregrounds to look at, it would, by an inevitable process of natural selection, develop into a non-achromatic instrument.

Summary and Recapitulation.

44. I would conclude therefore :—

(α) That the muscular sensation of the adjustment to focus of the lenses of the eye affords a possible means of estimating distances.

(β) That when binocular methods, and those depending on association of visible form or magnitude fail, the eye falls back on colour as a means of estimating distance.

(γ) That estimates of distance founded on apparent magnitude are liable to be rendered fallacious by the colour of the object.

(δ) That, conversely, estimates of distance founded on colour are liable to be confused by apparent magnitude.

(ε) That colour may in some cases outweigh, as a criterion, the evidence of binocular vision.

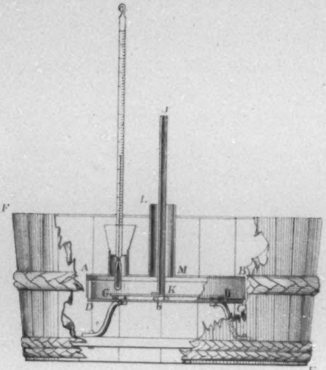
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Fig. 1.
Ice as an Electrolyte.

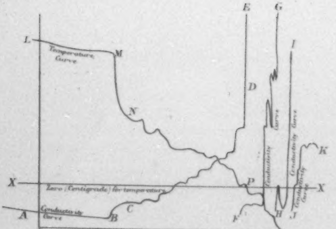


Fig. 2.

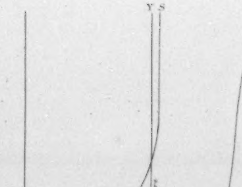


Fig. 3.

Mintern Bros lith

(ζ) That the chromatic aberration of the eye accounts for the universal opinion of painters as to the "retiring" character of blue, and the "advancing" character of red tints.

(η) That Aerial Perspective in Art is a true expression of a physical fact in the perception of distance.

University College, Bristol,
May 8, 1877.

XVI. *Ice as an Electrolyte.* *By* W. E. AYRTON *and* JOHN PERRY, *Professors in the Imperial College of Engineering, Tokio, Japan.*

[Plate III.]

FOR the purpose of measuring the resistance of ice at various temperatures, its power to act as an electrolyte, and its specific inductive capacity, the following piece of apparatus was constructed. A B C D (Plate III. fig. 1) is a copper box 17·4 centims. in diameter, rigidly fixed by means of three legs in the inside of a wooden tub F F. Resting on the bottom of the copper box, but separated from it by three small pieces of glass (*a*) (*b*) (*c*), is a copper disk, G H, 13 centims. in diameter, to which is fastened a copper strip J K. The box is closed by a very tightly fitting cover furnished with two openings—one, L M, to allow J K to pass through without touching the cover, the other for the admission of a thermometer. Distilled water having been introduced into the copper box to a sufficient depth to cover the disk G H, the temperature could be lowered by the introduction of a freezing-mixture of snow and salt inside the tub above and below the copper box, great care being taken that none of the mixture fell into the box through the tube L M, which was necessarily left open.

I. *Preliminary experiments.*—The current from one Meidinger cell was passed through the ice and a reflecting-galvanometer, the space between the copper plates being 2 millims. Keeping the temperature nearly constant (it varying between $-18^\circ{\cdot}2$ and $-17^\circ{\cdot}2$ C.), we found that in one hour the galvanometer-readings increased from 46·8 to 168·8, corresponding to a diminution in resistance per cubic centimetre of the ice from

354 megohms to 98 megohms. The cause of this may have been that, with such thin glass separating the copper disk from the box, some tilting may have occurred at freezing, so that the coppers were not perfectly parallel; or it may have been due to a very little of the salt water of the freezing-mixture having found its way into the copper box by passing between the box and the cover. The box was therefore opened and cleaned, fresh distilled water put in, and the cover cemented to the box by "cap-cement" to avoid the possibility of the salt water entering the box.

II. The current from eighty-seven porous Daniell's cells joined in series was passed through the ice, the temperature being kept very nearly constant at $-8^{\circ}\cdot0$ C. The galvanometer-reading fell regularly from 28·5 to 12·73 in twenty-seven minutes, being equivalent to an apparent rise in the resistance per cubic centimetre of the ice from 3767 megohms to 8443 megohms. The temperature remaining constant, the reading fell to 7·20 in about two hours, corresponding with a specific resistance of 17,310 megohms. Disconnecting the battery and joining the coppers on the two sides of the ice through the galvanometer, a discharge-current, which rapidly diminished, was obtained, as was to be expected.

Further experiments showing the difficulty of maintaining the copper disk approximately parallel to the bottom of the box, the three pieces of glass were removed and thicker pieces, 0·324 centim. thick, put in their place. The cover was again cemented to the box, this being, in fact, always carefully done after each occasion on which it was necessary to open the box.

III. Temperature being $2^{\circ}\cdot4$ C., an electromotive force of 0·0087 volt gave (after waiting eleven minutes to allow the current to overcome any previous polarization) a deflection of 212, corresponding with a resistance of 355,000 ohms per cubic centimetre. Allowing the temperature to fall slowly, we found the readings to remain pretty steady for thirty-four minutes when the temperature had become $-0^{\circ}\cdot6$ C. From this time there was a moderately rapid increase of resistance up to 14 megohms per cubic centimetre after forty-three minutes, the temperature now being $-3^{\circ}\cdot8$ C. The deflection was now 54; and we increased the battery ten times, when it was found that this increase of the battery did not increase the deflection proportionately (although subsequent experiments showed that the deflection was very approximately proportional to the current); in fact, making the battery ten times as large (that is, now using an electromotive force of 0·087 volt), only gave a deflection of 129. The battery was now immediately reduced to an electromotive force of 0·0087 as before; but the deflection was now only 28. Leaving on this electromotive force, the deflection was observed to steadily diminish until at last it became negative; and it eventually required an electromotive force of 0·0435 volt to bring the spot of light to zero. This electromotive force in the ice, which appeared to be developed by the employment of an electromotive force of 0·087 volt for only about one minute, remained quite constant, and continued to balance an electromotive force of 0·0435 volt for about half an hour, when, the apparatus having been cooled down, a larger electromotive force was now employed.

An electromotive force of	gave a deflection of	at a temperature of
0·087 volt	9·5	−5°·1 C.
0·174 ,,	19·5	
0·261 ,,	27·7 diminishing to 23·5 in thirteen minutes	−6°·4 C.

These deflections are nearly proportional to the electromotive forces.

An electromotive force of 2·61 volts	gave a deflection of 52·5 diminishing to 30·1	at a temperature of −8°·3 C.
Now suddenly increasing this to 4·35 volts	the deflection diminished to 39·5	−8°·3 C.

It might have been expected that doubling the electromotive force would have more than doubled the deflection, since the diminution of resistance in a dielectric produced by time of charging only proceeds gradually—whereas the deflection only increased from 30·1 to 39·5. This peculiarity is shown more fully in the following Table, in which the readings just before and after changing the battery-power are given, the intermediate ones being omitted:—

Electromotive force 2·61 volts.

Time.			Deflection.	Temperature.
h	m	s		
7	48	30	30·1	−12° C.

Electromotive force of battery increased to 4·25 volts.

7	49	30	39·5	−12° C.
7	51	30	36·5	

Electromotive force increased to 8·7 volts. First swing off the scale, but very soon grew steady on returning.

7	52	0	53·1	−12°·2 C.
7	53	0	50·5	
7	54	0	49·1	

Electromotive force increased to 17·4 volts. First swing off the scale.

7	55	0	72·7	−12°·5 C.
7	56	0	69·0	
7	61	0	59·5	

Electromotive force increased to 28·71 volts. First swing off the scale.

8	2	0	76·5	−12°·8 C.
8	5	0	68·6	
8	6	0	67·2	−13°·0 C.

Short-circuited the coppers on the two sides of the ice for four minutes.

Afterwards electromotive force increased to 87 volts. First a great swing off the scale, then returned, and in about one minute—that is, at

h	m	s	Deflection.	Temperature.
8	12	0	212·7	−12°·85 C.
8	15	0	145·7	
9	12	0	66·2	−10°·8 C.
9	17	0	65·2	
9	58	30	66·2	− 8°·85 C.

Comparing the observation at $8^h\ 12^m\ 0^s$ with that taken at $8^h\ 6^m\ 0^s$, we see that the deflections are nearly proportional to the electromotive forces employed; this, however, is not the case in the other instances when the electromotive force was increased. The object of giving three or four time-observations for each electromotive force in the above Table is for the purpose of showing with what rapidity the reading was changing in each case.

IV. *February* 11.—A very consistent series of observations was made. We first tried the effect of varying the time of charging when measuring the discharge from the arrangement as a condenser; and we found that increasing the time of charging increased the discharge, the temperature of the distilled water in the copper box being 8°·7 C. Charging, however, for ten seconds with an electromotive force of 0·174 volt, and discharging through the galvanometer when shunted with the one-thousandth shunt, and leaving the copper disk and box short-circuited for fifteen seconds after each discharge, we obtained, during many successive trials, swings varying between 75 and 81, and having a mean value of 79. This corresponded with a capacity for the water of 1881 microfarads, or 4·384 microfarads per cubic centimetre, making the specific inductive capacity of water 50×10^6, that of air being called unity. Of course this number is rather too low, as no allowance is made for the loss of charge that must occur in the very short interval between the conclusion of the charging and the commencement of the discharge. The current produced by an electromotive force of 0·174 volt was now passed through the water, and the fall of current measured as the temperature was lowered. This diminution of current was partly due to polarization, but more due to increase of resistance by diminution of temperature. It was quite evident that this increase of resistance was very great, and that it was quite regular in the passage from the liquid to the solid state. These observations we do not give; it is sufficient to state that they were consistent with the more important subsequent observations given below. When the temperature had fallen to −13°·5 C., we stopped the resistance-tests to take the capacity of the ice. We charged for ten seconds with an electromotive force of 0·174 volt, and short-circuiting the ice for fifteen seconds after each discharge, exactly as was done with the water. We now found, however, that when using the one-thousandth shunt there was no visible motion of the spot of light on discharging; and when no shunt was employed the swings only reached 25. Now, disregarding the error produced by varying the shunt in capacity-testing (a correction for which could be made in the way explained by Mr. Latimer Clark, Journ. Soc. of Teleg. Engineers, vol. ii. 1873, p. 16), and also neglecting the frictional resistance of the air, it follows that the capacity of ice at −13°·5 C. is to the capacity of water at +8°·7 C. as 25 to 79,000, or as unity to 3160. This result, however, has to be corrected for the effects of an opposing electromotive force due to some slight oxidation of the copper on the sides of the ice, and which equalled 0·053 volt. Applying this correction, we find the ratio of the capacities to be as unity is to 2240. This makes the capacity per cubic centimetre of ice at −13°·5 C. to be 0·002 microfarad, and the specific inductive capacity 22,160, that of air being called unity.

Substance.	Approximate capacity per cubic centimetre in microfarads.	Specific Inductive capacity approximately.
Air	8831×10^{-11}	1
Ice at −13°·5 C.	196×10^{-5}	22160
Distilled water at +8°·7 C.	4·384	50×10^{6}

This furnishes an additional example of the principle recently pointed out by us, that *low* specific resistance is associated with *high* specific inductive capacity.

For further experiments on the capacity of the ice at different temperatures &c., see further on.

At 12 hours 30½ minutes the current produced by 2·61 volts was passed between the copper plates, the ice being at a temperature of −13°·6 C. The temperature was allowed to rise very gradually; and time-readings of the galvanometer deflection were taken. From these the curves A B C D E, F G, H I, J K (fig. 2) have been constructed, horizontal distances representing time on such a scale that from the point A to the point E the time was 207½ minutes, and vertical distances measured from the line O O to the curve A B C D E representing conductivity, the specific resistance per cubic centimetre at B, for instance, being 2240 megohms. F G is a continuation from E one tenth as great for vertical distances (that is, for conductivity), but on the same scale for horizontal distances. Again H I is a continuation from G on a scale one hundredth as great for vertical distances as in the curve A B C D E, and J K on a scale for vertical distances one thousandth as great, the scales for horizontal distances in all the curves being the same. The curve L M N P Q is drawn so that vertical distances measured from the line X X represent temperature, and horizontal distances time—the zero for time, and the length corresponding with one minute, being the same as for all the other curves; negative temperature is represented upwards and positive temperature downwards—the point L corresponding with a temperature of −13°·1 C.

The current continued to diminish regularly to the point B, when the temperature shown by the point M was −12°·3 C., and the time 10 minutes past 3. At this point and at the other steep places in the curves, water was thrown into the freezing-mixture to raise its temperature; and at such points as C, where the current had evidently reached a maximum at a corresponding temperature N, the readings are supposed to represent the true conductivities at the corresponding temperatures; but this, of course, is only approximately accurate. It is very striking how the maxima of conductivity and temperature correspond with one another, considering that the thermometer only indicated the temperature of the air in the copper box above the ice, whereas change of current indicates change of state in the ice itself. The very great increase in conductivity which occurs at the melting-point is seen to be quite regular, and unlike what one might expect from the discontinuity of the solid and liquid states.

Taking the corresponding conductivities and temperatures at points C, N, &c., we have drawn the curves R S, T V (fig. 3). Horizontal distances to the right of Y Y represent positive temperatures, and to the left negative, on such a scale that the point R corresponds with a temperature of −12°·4 C. Vertical distances measured from X X represent conductivity on such a scale that the point R corresponds with a resistance per cubic centimetre of 2240 megohms. T V is a continuation from S on a scale for vertical distances three thousandths of that employed in the curve R S, the scale for temperature remaining as before: the point V thus corresponds with a resistance per cubic centimetre of 0·33 megohm at a temperature 11°·02 C. From the curves (fig. 3) it would appear that the very great increase in conductivity occurred at about 1° C.; it is possible, however, that the apparently corresponding points of maximum temperature and maximum conductivity shown in the curves (fig. 2) may not have really exactly corresponded, although changes in the temperature always accompanied changes in the current.

The curves R S, T V do not appear to be logarithmic. The coordinates of the points from which they have been drawn are given in the following Table:—

Temperature, in degrees Centigrade.	Resistance per cubic centimetre, in megohms.
−12°·4	2240
− 6·2	1023
− 5·02	948·6
− 3·5	642·8
− 3·0	569·3
− 2·46	484·4
− 1·5	387·6
− 0·2	284·0
+ 0·75	118·8
about + 2·2	24·8
+ 4·0	9·1
+ 7·75	0·54
+11·02	0·34

V. The copper disk G H (fig. 1) was now removed and replaced by a disk of zinc of exactly the same size. The pieces of glass used to separate the zinc disk from the bottom of the copper box were the same as those previously employed, being 0·324 centim. thick. Distilled water was poured in so as to cover the zinc plate, and the cover was cemented on the box as before. In the following experiments, K J (fig. 1) was a strip of zinc cut out of the same sheet as the disk G H and bent up: the strip K J and the disk G H were therefore continuous without joint. The point J was joined to one of the electrodes of a Thomson's quadrant electrometer, and the copper box D C to the other electrode. Both with water and with ice the maximum electromotive force obtained was one volt about.

In the first sets of experiments, A, B, C, the zinc disk and copper box were alternately joined together and insulated from one another, the result of the short-circuiting being, of course, to diminish the electromotive force by polarization. While this was being done the temperature was gradually lowered. It is rather difficult to determine how much the results were affected by polarization and how much by the lowering of the temperature. We give, however, the results (in a tabulated form) as we obtained them:—

A.

Time of short-circuiting, in minutes.	Deflection immediately on insulating.	Highest deflection.	Time taken to arrive at highest deflection, in minutes.	Temperature, in degrees Centigrade.
¼	......	240	1st time quickly 2nd time slowly	about 0°
¼	......	240	3	−4°
¼	......	207	2	falling gradually.
¼	.....	203	......	
¼	......	196	......	
¼	......	190	......	
¼	......	178	......	
3	......	176 diminishing to 89	quickly.	−12°
		B.		
1	nearly 0	210	8	15° to 1°·5
1	,,	151	9	−1° to −5°·5
1	,,	170	...	−6°
		C.		
1	184	203	5½	+2°·6
1	184	203	5½	+2°·6
3	168	204	...	+2°·6
7	156	204	...	+2°·6
10	150	167	1	−1°·5 to −2°·7
1	153	175	6	−3° to −3°·5
3	154	179	7	
7	......	195·5	25	−5° to −9°·5
7	......	208·5	60	−12°

It is possible that the deflection 208·5 would always have been obtained had the zinc plate been left sufficiently long insulated after short-circuiting. The plate and box, however, were always short-circuited when the rise in the electromotive force had apparently ceased.

To separate, to a certain extent, the effects due to polarization from those due to difference of temperature the following experiments were made. The zinc plate and copper box were alternately short-circuited for two minutes and insulated for two minutes, the temperature being kept constant at $+22^{\circ}\cdot5$ C. This being repeated six times, reduced the deflection 231, obtained at the end of the first two minutes of insulation, to 155, obtained at the end of the last two minutes of insulation. Exactly the same experiment being repeated ten times with ice at a constant temperature of about -17° C., the deflection 212, obtained at the end of the first two minutes of insulation, was only reduced to 203 at the end of the last two minutes of insulation. It would therefore appear from this set of experiments, that the smaller amount of polarization produced by the high resistance of the ice only allowing a small current to flow during the short-circuiting of the zinc plate and copper box was of rather more importance than the solidity of the ice retarding dissipation of polarization.

VI. *Further experiments on the Specific Inductive Capacity of Ice.*—The zinc disk G H (fig. 1) was now removed and the original copper disk replaced. With a charging electromotive force as small as 0·174 volt, we found that, in the case of ice, it was always necessary to carefully correct the swing for the opposing permanent electromotive force existing between the copper disk and the copper box, whereas with water at about $+10^{\circ}$ C., when using the same charging electromotive force, it was not necessary to make any such correction. Rough measurements gave this opposing electromotive force at $-12^{\circ}\cdot4$ C. as 0·017 volt, and showed that as the temperature rose there seemed to be a regular decrease: at 0° C. it was only 0·003 volt, and at higher temperature it was immeasurably small by the rough method we employed. To avoid this correction being of so much importance, we used an electromotive force of 0·87 volt to determine the capacity of ice at different temperatures. We did not find that the time of charging or the time of short-circuiting affected our results nearly as much as in the case of water; in fact, the time of short-circuiting our ice condenser between successive tests of its capacity hardly affected the results at all; but during a series of observations, the time of short-circuiting between every two being fifteen seconds, and the time of charging being gradually increased from five seconds up to thirty, the swings increased from 56 to 70 divisions of the scale. We therefore, as on the former occasion, always charged for ten seconds and short-circuited for fifteen. Four or five consecutive observations of this kind always showed a slight increase from the first to the last, the temperature being kept quite constant. Several series at different temperatures are shown in the following Table:—

Time.	Temperature, in degrees Centigrade.	Swings, first and last of a series of four.
h m	°	
9 20	−9·5	61 61·5
9 25	−8·8	57 61
9 30	−7·7	58 60·5
9 37	−3·5	57 62·5
9 44	−2·5	60 61
9 55	0	47·5 52·5

In the above experiments the ice condenser always remained short-circuited while the temperature was being raised between each set of experiments. The results obtained appear to show that the specific inductive capacity of ice does not materially alter from −9°·5 C. to −2°·5 C.; the apparent change near the melting-point is very probably due to the increased conductivity of the ice allowing much of the charge to be lost before the discharge through the galvanometer. Our preceding experiments have shown that the conductivity of $\left\{\begin{matrix}\text{ice}\\\text{water}\end{matrix}\right\}$ increases regularly *without discontinuity* from −10° C. to +10° C., although altering very rapidly at 0° C., where the change of state occurs. The specific inductive capacity, on the other hand, appears to change very little while the dielectric (ice) is solid, and perhaps also changes very little while the dielectric (water) is liquid. It must therefore probably undergo a great change at the melting-point, since we have shown that the specific inductive capacity of water at 8°·7 C. is about 2240 times that of ice at $-13^\circ\!\cdot\!5$ C. The specific inductive capacity seems therefore to be a stress and strain phenomenon, and to be intimately connected with the rigidity of the body; whereas the connexion between conductivity and rigidity seems to be less marked. This, we think, bears out all recent theories in molecular physics. The complete investigation of the connexion between the conductivity and specific inductive capacity of $\left\{\begin{matrix}\text{water}\\ \text{ice}\end{matrix}\right\}$ at different temperatures will form the subject of a second paper.

March 22, 1877.

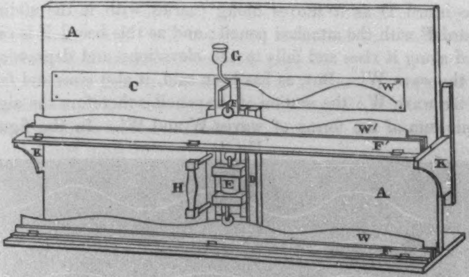
XVII. *On an Apparatus to illustrate the Interference of two Plane Waves.* *By* C. J. Woodward, *B.Sc.*

The effect produced by the simultaneous propagation of two or more plane waves is in a few simple cases easily realized; in others, however, the mind is somewhat harassed in ascertaining what will be the resultant wave made up of certain given elements. The apparatus I am about to describe is intended to assist the student by enabling him to draw for himself the required resultant wave; or the apparatus may be used in the class-room to illustrate the general subject of interference.

So far as I know, the only apparatus of the kind in use by lecturers is one based on the method described by Dr. Young (Natural Philosophy, Lecture xxxiii.); but here, to obtain any variety of effects, a series of dissected waves are required, and these are troublesome to make or expensive to purchase; whereas with the arrangement I now exhibit to the Society, when once the framework of the apparatus is made, combinations of any desired waves may be drawn, with merely the trouble incidental to cutting out the required waves in cardboard or thin tin.

The apparatus consists of a board, A A, about 3 feet long, 2 feet wide, and 1 inch thick, set upright on a base-board B. A strip of cardboard, C, is fastened by drawing-pins to the board; and on this is drawn the compound wave resulting from the two component waves W, W′. These component waves are cut out of strong cardboard or tin, and can be easily and quickly placed in position by letting down the flaps F, F′. D is a stout mahogany board, with a wedge-shaped groove in it sufficiently wide to allow the board E to slide freely up and down. A handle, H, is secured to the board D to enable the operator to move D from one end of A to the other. The board E has a pulley fastened to its lower part; and this pulley runs on the tin wave W, so that if the board D be moved horizontally, the sliding board E will rise and fall as the pulley passes over W; and of course, were there a pencil attached directly to E, the pencil would trace a curve the same, or very nearly the same, as that of the wave. The sliding board E has also a wedge-shaped groove cut in it to allow the board F to slide vertically; and to F is also attached a pulley, which runs on the wave W′. With the upper board F, as with the lower, if the pulley be made to traverse the wave W′, a pencil fastened to F would trace a wave corresponding to W′. The pencil (or, more properly, pen) used in the apparatus consists of a thistle-funnel, with the tube drawn out so as to have an

Fig. 1.

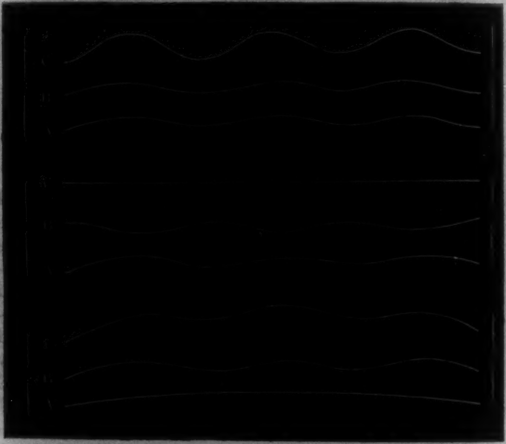


Moving the boards D, E, F from right to left by means of the handle H traces the wave W″, a combination of the waves W and W′.

opening of only a fraction of a millimetre. The tube is bent as shown in the figure at G; and the drawn-out part presses gently against the cardboard C. To charge the pen, some violet ink is poured into the thistle-funnel, which is then closed with a cork.

The action of the apparatus will easily be understood. As the board D moves along, the board E rises and falls; and this by means of a roller causes the wave W′ to rise and fall to each elevation and depression of the wave W below. Now the board D as it moves along carries with it the sliding board F with the attached pencil; and as this board F is carried along it rises and falls to the elevations and depressions of the wave W′. But, as has been said, it also rises and falls to the wave W: the motion of the pencil is therefore the algebraic sum of the forms of waves W and W′. In the figure the waves W and W′ are of the same length and amplitude and correspond in phase, so that the tracing W″ is a wave of the same length but twice the amplitude of the waves below.

Fig. 2.



The wave C results in each case from the superposition of the waves A and B immediately below C.

By moving the wave W′ to the right, its phase may be made $\frac{1}{4}$, $\frac{1}{2}$, &c. of an undulation different, and a fresh tracing obtained. By removing the wave W′ and inserting successively others of different lengths and amplitudes, various combined waves are traced out on moving the board D along. A few tracings obtained by the apparatus are represented in fig. 2, page 184.

In order that the frame carrying the wave W′ may rise and fall freely, the brackets K, K are linked together at the back of the board by a parallel motion, used in the Cowper printing-machine, and which will be found described in Goodeve's 'Elements of Mechanism,' 3rd edit. page 66.

It is obvious that by an extension of the same principle an apparatus could be made to give the tracing of a combination of three or more waves. To do this, however, the mechanical arrangements must be much better than in the comparatively rough instrument I have exhibited.

XVIII. *On Interference Fringes within the Nicol Prism.*

By Silvanus P. Thompson, *B.Sc., B.A.**

1. In the 'Edinburgh New Philosophical Journal' for 1828 (p. 23) is a communication "On a Method of so far increasing the divergency of the two Rays in Calcareous Spar that only one Image may be seen at a time." In this, the original account by the inventor of the now well-known Nicol prism, occurs the following sentence:—"There is a tinge of blue where the ordinary ray vanishes on one side, and a tinge of orange accompanied by a number of obscurely coloured fringes, where it terminates on the other." Probably the great majority of those who are familiar with the Nicol prism are acquainted with the phenomena alluded to in the passage quoted. As the author has not found, however, any more explicit reference to them, nor any attempted explanation of them, he ventures to offer the following account of an examination he has made of their nature and origin.

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* Read June 9, 1877.

General Description of the Phenomena.

2. Let a Nicol prism* be placed so that its axis is in a line with the axis of the eye, with the longer diagonal of the lozenge-shaped field vertical, and so that the oblique face of the spar retreats from the eye from left to right. If then the eye be moved so as to explore the visible interior, it will be seen that the light of the "field" (which, it will be observed, is that of the ray now usually called the extraordinary ray) is terminated to the left by a margin of violet-blue light running vertically in almost a straight line, having the violet edge to the left, next the darkness, and the blue and bluish-green portion to the right, next the light. Further, this field is terminated to the right, not by the "orange band" and fringes, but simply by the limits of the edges of the prism.

3. The "orange band" is situated at the termination of a second "field" of less intense illumination, which only comes into view when the light passes to the eye obliquely through the prism. This is the field of the "ordinary" ray; as may be proved by first passing the light directly down the axis of a second Nicol prism also having its longer diagonal vertical, when the second field, together with the orange band and fringes, disappears totally. The "orange" band consists of red, orange, and orange-yellow rays, the former lying more to the left, the latter more to the right. The fringes, which, with an important modification, present the colours of Newton's transmitted rings, lie right within the coloured band, and extend beyond it parallel to its edge. They are curved in form, the sinus of the curve being toward the right. The visible curvature is greater the nearer the eye is brought toward the prism. Their form approximates to that of the arc of a circle; though really only a portion of a conchoid curve which becomes at last asymptotal to a line varying with the position of the eye. Could the eye be actually plunged within the substance of the Nicol prism, the curves would, as will hereafter be indicated, appear truly circular in form.

* My experiments have been made chiefly with two Nicol prisms, by Tisley and Spiller, of 1 inch clear aperture each, and with a larger prism of $1\frac{3}{4}$ inch aperture; but the phenomena may be observed with any Nicol prism whatever.

4. When monochromatic light is employed, the fringes in the "orange band" become more numerous and sharper; and a second set of fringes, not otherwise noticeable, appears within the edge of the "blue band:" these fringes are precisely similar in kind with those of the "orange band," but their curvature is usually so slight as to be unobserved. If a thin prism of glass of suitable angle be interposed in the path of the ordinary ray, the particular dispersion of the "orange band" may be corrected, and the fringes are then left sharper and brighter; the second bright band of the fringes is the brighter. The glass prism may be employed either between the eye and the Nicol prism, or beyond the Nicol prism, in this experiment. The particular dispersion of rays that produces the "blue band" may also be corrected by a glass prism, but only when this is placed between the eye and the Nicol prism, not when beyond the Nicol. When the blue band is thus eliminated, the fringes observed in monochromatic light may be seen at the termination of the field of the extraordinary ray to the left. The fringes of both sets appear narrower in blue light than in red light.

5. The light which gives the extreme red portion of the "orange band" meets the first surface of the Nicol prism at an angle of about 18° 15′ with the axis of the prism, passes through the prism almost parallel to its axis, and emerges parallel to its former path. It, and in fact all the rays of the second "field" (that consisting of ordinary rays, and seen obliquely), suffer therefore a lateral displacement. The light of the extreme violet ray of the "blue band" meets the first surface of the prism at an angle of about 80°, and it and most of the rays of the bright "field" (that seen directly, and consisting of "extraordinary" rays) pass almost in straight lines through the prism, and emerge without suffering deviation or any considerable displacement. The extreme violet ray makes an angle of about 9° with the axis of the prism.

6. If the light of the "blue band" be received upon the horizontal slit of a spectroscope, the presence of dark interference-stripes reveals the character of the light of that region of the field.

Cause of the Phenomena.

7. The two sets of fringes—those of the "orange band" and those of the "blue band"—are due to interference taking place within the film of "balsam" at the critical angle of total reflexion for ordinary and extraordinary rays respectively. The production of interference-phenomena in a thin film placed beneath a prism of a more highly refractive substance, and occurring just within the limit of total internal reflexion of the prism, was first observed by Sir W. Herschel, and is described in detail by Sir John Herschel in his 'Essay on Light,' art. 641. It is there shown that, to an eye immersed in the prism, an iris is formed at the edges of the cone of rays which reach the eye at the critical angle, and that this iris is blue for reflected, red-orange for transmitted rays; the separation of the colour being the simple consequence of the total reflexion following the index of refraction, which, being higher for more refrangible rays, causes them to meet the eye in a cone of lesser angle. The fringes seen within the red-orange iris that thus borders the limiting circle of transmitted rays follow naturally from a consideration of the paths travelled by the various rays in their passage through the thin film below. They follow the order of Newton's rings, except that those nearest to the limit are deprived of the rays of higher refrangibility within whose critical angle they lie; but the regularity of their form and tint is disturbed, to an eye outside the prism—the cone being distorted and the circularity of the arcs destroyed, and the fringes being displaced and confused by dispersion at the outer surface of the prism.

This experiment of Herschel's is usually made with an equiangular prism and a piece of plate glass pressed against its base. The width of the fringes increases with pressure as the thickness of the film of air diminishes. As the critical angle depends on the index of refraction out of the film into the prism, the cone of rays has a wider base when a film of water is used instead of a film of air; and the nearer the index of the film to that of the prism, the greater becomes the radius of curvature of the iris and fringes.

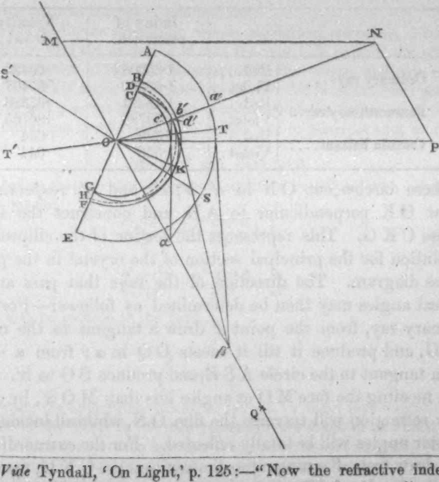
Of the Conditions of Total Reflexion.

8. In order to apply the case of the iris and fringes observed

by Herschel to the phenomena of the Nicol prism, it will be necessary next to prove that, at certain angles of incidence, both the ordinary and extraordinary ray suffer total reflexion at the surface of the separating film.

Most text-books assert, on the contrary, that total reflexion of the ordinary ray does not occur*. The original paper of Nicol spoke only of *increasing the divergency between the two rays*; and it was left to the late Mr. H. F. Talbot to point out† that both rays came through at a certain obliquity, but that one image vanishes by total reflexion *before* the other.

9. The following modification of the construction of Huygens will enable us to establish the correctness of Mr. Talbot's statement. Let the parallelogram M N P O represent a principal section through the axis of the Nicol prism, O and M



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* *Vide* Tyndall, 'On Light,' p. 125:—"Now the refractive index of Iceland spar is for the extraordinary ray less, and for the ordinary ray greater than for Canada balsam. Hence, in passing from the spar to the balsam, the extraordinary ray passes from a less refracting to a more refracting medium, where total reflection cannot occur;" &c.

† "Facts relating to Optical Science, No. II. On Mr. Nicol's Polarizing Eyepiece," Phil. Mag. 1834, p. 289.

being the two ends of the shorter diagonal of the lozenge-shaped face. O N represents the trace upon this plane of the film of balsam, making an angle of about 20° 40′ with O P. Produce O M to Q. Through O draw a line A O E parallel to the direction of the optic axis of the crystal, making an angle of about 47° with O M. About O as centre describe three semicircles having radii O A, O B, O C, respectively proportional to the velocity of light in air and in the extraordinary and ordinary rays of calc-spar. Draw another semicircle with radius O D proportional, on the same scale, to the velocity of light in Canada balsam. The following Table gives these values (air =1), together with the corresponding indices of refraction for red and violet rays (rays B and H of Fraunhofer):—

		Index of refraction.	Velocity (air =1).
Ordinary ray......	Red....	1·65308	·60493
	Violet..	1·68330	·59407
Extraordinary ray...	Red....	1·48391	·67386
	Violet..	1·49780	·66765
Canada balsam....	Red....	1·529	·654
	Violet..	1·553	·644

These circles cut O N in a', b', c', and d' respectively. Draw O K perpendicular to A E, and construct the semi-ellipse C K G. This represents the section of the ellipsoid of revolution for the principal section of the crystal in the plane of the diagram. The direction of the rays that pass at the critical angles may then be determined as follows:—For the ordinary ray, from the point d' draw a tangent to the circle C c' G, and produce it till it meets O Q in α; from α draw α S a tangent to the circle A S E, and produce S O to S′. All rays meeting the face M O at angles less than M O S′, by ordinary refraction will traverse the film O N, while all incident at greater angles will be totally reflected. For the extraordinary ray, draw from d' a tangent to the semi-ellipse C K G, meeting O Q in β; draw β T a tangent to the circle A S E, join T O, and produce to T′. All rays incident on the face O M, within the angle M O T′, and entering by extraordinary refraction, will be transmitted, but those incident at greater angles will be totally reflected. Hence the true "field" of the Nicol prism, in which only the extraordinary rays are found, is that of rays incident within the angle S′ O T′. Supposing that we have hitherto taken the indices of refraction for red rays in our construction, these angles will determine the limits of transmission for red rays. If now new circles be drawn* having the values of O B, O C, and O D to correspond to violet rays, and a new semi-ellipse be drawn as before, the same construction will be found to give slightly different positions for the lines O S′ and O T′. For violet the limiting angle for ordinary rays is rather less than M O S′, and for extraordinary rays rather greater than M O T† (not shown in small diagram).

10. It is well known that the refractive index varies in dif-

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* This has not been attempted in the diagram, as an inconveniently large scale would have to be chosen, and then the construction would be confusing without the use of coloured lines.

† It can readily be shown, on simple algebraical reasoning, from the data given, that the circle D d' H cuts the line O N outside the ellipse. Call r the portion of line O N intercepted by the ellipse, and call angle A O N, θ. This angle never exceeds 48° 25′, and is less in some prisms. Taking x and y as the rectangular coordinates of the intersecting point, when the ellipse is referred to O as origin and to principal axes as coordinates,

$$x=r\sin\theta \text{ and } y=r\cos\theta.$$

Substituting these values in general equation to ellipse with origin at centre, we get

$$\frac{r^2\sin^2\theta}{a^2}+\frac{r^2\cos^2\theta}{b^2}=1,$$

and

$$\frac{b^2\sin^2\theta}{a^2b^2}+\frac{a^2\cos^2\theta}{a^2b^2}=\frac{1}{r^2},$$

which may be reduced to the form

$$r=\frac{a}{\sqrt{\sin^2\theta+\frac{a^2}{b^2}\cos^2\theta}}.$$

Inserting the appropriate values for red and for violet rays respectively, as given in the Table in § 9, the values of r are found to be 0·6369 and 0·6247, which are severally less than the respectively corresponding values of the radius O d', 0·654 and 0·644. In either case, therefore, a tangent to the ellipse can be drawn from d', that is to say, it is possible for total reflexion to occur to each ray; and there is consequently in the Nicol prism an obliquity of incidence at which both rays are transmitted, another obliquity at which, while the extraordinary is transmitted, the ordinary ray is reflected aside, and another at which both rays are totally reflected.

ferent specimens of Canada balsam. If one with too high a refractive index be taken, O D will approach O C in value, and then it may happen that d' will fall within the ellipsoid; in which case it will be impossible to draw a tangent, the corresponding fact being the impossibility of total reflexion at any angle. After carefully working this construction for the best determinations of the various refractive indices by Rudberg, Wollaston, and Brewster, the author has been unable to discover such a case. As, however, it is notorious that in the large Nicol prisms now manufactured ordinary Canada balsam cannot be employed, but a harder gum-resin, such a case may occur; but then there will be no "blue band" unless the point d' still falls without the ellipsoid for red rays.

Of the Red-orange Iris.

11. From the foregoing considerations it will now be apparent why a *red-orange* iris is seen at the limiting surface of the ordinary rays, for it has been shown that the limit for rays of high refrangibility lies within the angle M O S′; hence red and orange rays are transmitted at angles of incidence at which no blue or violet or green can pass.

Of the Blue Iris.

12. It will also be seen that if the limit for violet extraordinary rays lie beyond M O T′, violet and blue rays can be transmitted at angles at which red and orange rays are cut off. Hence the iris at the limiting angle will be blue, not orange. It will not be forgotten that O T is incident at about 80° to O M, at which angle the ray would suffer little deviation and dispersion; but this deviation and dispersion is in reality from, not towards, the normal to the surface, since the crystal is negative and the ray extraordinary; so that the dispersion is reversed for rays entering at angle M O T′.

A simple experimental proof of this reversal of dispersion is obtained by looking through a Nicol prism at a narrow opaque body against the light, when slight tinges of blue and of yellow appear at their edges; but the positions of these blue and yellow margins are reversed in the two fields.

The blue iris is not so much curved as the orange iris, since the index of the balsam of the film is nearer to that of the extraordinary ray than of the ordinary ray. For the same reason the cone of rays coming to the eye must be more obtuse, and hence, for the same thickness of film, the interference-fringes must be nearer together and finer; they will therefore be the more easily obliterated in the subsequent dispersion at the face of the prism nearest the eye, as in fact is the case, except when the dispersion is corrected by a thin glass prism, or avoided by the use of monochromatic light.

University College, Bristol,
May 21, 1877.

Note.—In Foucault's prism, where both rays are totally reflected at the surface of a film of air, instead of balsam, the angular magnitudes of the limiting cones of transmitted rays are much less, and the field is consequently narrower. Moreover, as the extraordinary ray in this case suffers total reflexion when the limiting angle of incidence is much greater than in the Nicol prism, the deviation and dispersion are toward the normal to the surface, and there can be no blue iris. In the Foucault prism, in fact, a series of coloured bands and fringes exists at the limit of each of the two fields, but each is red-orange.—S. P. T.

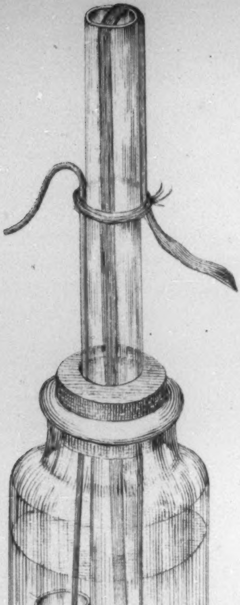

Fig. 1.

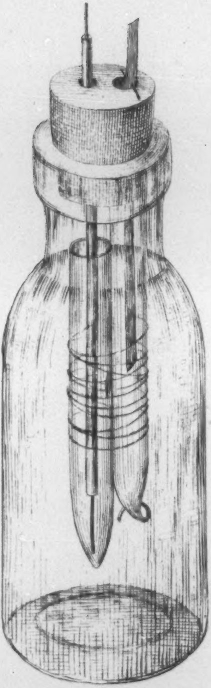

Fig. 2.

Mintern Bros lith.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

JANUARY 1878.

XIX. *On a Form of Daniell Cell convenient as a Standard of Electromotive Force.* By OLIVER J. LODGE, *D.Sc.**

[Plate IV.]

ALTHOUGH a volt is the formal unit of electromotive force, yet it happens in practice that differences of potential get stated as equal to so many Daniell cells more frequently than any thing else, showing that there is some decided convenience in this mode of statement, a convenience partly owing, no doubt, to the fact that a freshly set-up Daniell is a tolerably uniform and easily reproduced standard. An ordinary Daniell, however, is by no means suitable as a standard, because of the diffusion of the copper-liquid through the porous cell. This defect must obtain in any cell where two liquids separated by a porous partition are employed; and hence attempts have been made to construct standard cells with solid electrolytes, or with mercury instead of copper salts, as in the little cell devised by Mr. Latimer Clark, which, though not absolutely constant, is still, I suppose, the best for its special purpose. But all cells with solid electrolytes are extremely inconstant, in the sense that they suffer greatly from short-circuiting and take some time to recover themselves; and there are some other inconveniences attending the use of a large number of Clark's cells.

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* One of the cells was exhibited at a meeting of the Society in February 1877.

A convenient Daniell Cell with high internal Resistance.

Of all known cells, a Daniell charged with sulphate of zinc and sulphate of copper seems to be the most perfect—in this respect, that the materials remain always the same during action except that the sulphate of zinc gradually increases in quantity, a difference which scarcely affects the electromotive force. Almost the only defect in the constancy of a cell so charged is due to the fact that the two liquids diffuse into each other, for which reason the battery cannot retain its original state after it has stood for some time. Any thing equivalent to a porous partition is quite useless for keeping the liquids separate; and the only plan seems to be to provide as long a column of liquid as possible for the copper salt to diffuse through.

This is done in a compact and simple manner in the cell represented in fig. 1 (Pl. IV.). A wide-mouthed bottle (or a tall jar) is fitted with a cork through which passes a wide glass tube open at both ends. To the lower end of this tube a short closed tube (like a test-tube) is tied with silk thread; a long strip of sheet zinc is put down the open tube; and a copper wire, recurved at the bottom and coated with sealing-wax except at its two ends, is passed through the cork to the bottom of the closed tube, where it is imbedded in a few crystals of copper sulphate. The bottle is then nearly filled with dilute sulphate of zinc, and the cork with the tube is inserted, the latter being so arranged that the end of the zinc strip and the mouth of the short tube are both below the surface of the liquid. In a short time a strong solution of sulphate of copper forms at the bottom of the closed tube where the copper wire is bare, and it gradually diffuses upward; but in order to reach the zinc it has to diffuse itself all through the water of the bottle and then up the long tube containing the zinc; and this takes a long time, though it certainly does take place to some extent in a week or so.

But when I want to put the cell by for any length of time, I pull the long tube a little higher up through the cork, so that the mouth of the short tube emerges above the liquid and thus entirely prevents diffusion. The zinc strip is also raised out of the liquid by the same action. It is convenient to have the cork fitting pretty air-tight; or else evaporation may go on from the edges of the tube, and the salts which crystallize there may continue the diffusion slowly.

The copper wire need not be covered with wax or any thing; but if it were not, its upper parts would assist in the action until they were polarized; and hence the internal resistance would be liable to vary, which is not desirable. The internal resistance of such a cell is always rather high: for instance, in the one of which fig. 1 is a portrait, the bottle stands about 6 inches high, and the internal resistance is about 500 ohms when arranged as shown; but of course it depends greatly on the position of the tubes, and also somewhat on the temperature. Hence it is not to be regarded as giving necessarily a very constant current, but rather as a cell which can be used for a long time and yet keep its electromotive force nearly unchanged.

I have also made a set of small cells on the same principle, with ordinary quilled tubing for the tubes, and with test-tubes for the containing vessels, making the connexions by twisting the thin copper wire of one cell round the projecting tube (with the zinc bent down springily over it) of the next. A large number of such cells may be quickly made and arranged in ordinary test-tube stands; and they are convenient for many purposes, such as capacity- or insulation-testing, where high electromotive force is required*. The whole rack of cells was once accidentally upset; but though a little liquid escaped from the open ends of the zinc-tubes, the copper-liquid remained steady at the bottom of its tube without visible disturbance.

A Cell for a Standard of Electromotive Force.

Fig. 2 shows a bottle about 3 inches high, which I have made to act as a standard of electromotive force. It differs in no essential respect from fig. 1, except that the mouth of the tube containing the copper-solution never dips below the surface of the liquid, but always projects ¼ inch above it. The

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[*] I suppose that by using platinum instead of copper wire, and strong nitric acid or else sulphuric acid and bichromate of potash instead of the copper salt, one could nearly double the electromotive force, though with some loss of constancy.

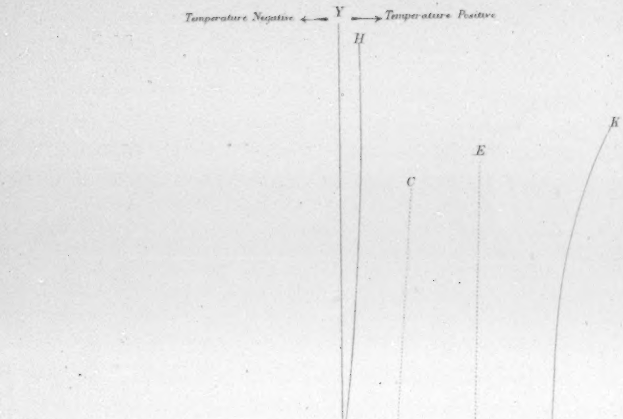
other or open tube does not project at all above the cork; and its lower end is drawn out and coiled round so as still further to retard the passage of the copper-liquid to the zinc. The zinc, which should be pure, is supported at the right height by a pin thrust through it. The closed tube is proportionally longer than in fig. 1; it is nearly filled with pure sulphate-of-copper solution, a few crystals being placed at the bottom; and it is tied to the other tube, as before, with silk thread (which appears not to rot). The copper wire is gutta-percha-covered with its ends bared. The bottle is filled nearly to its neck with very dilute sulphate of zinc; and the cork is then inserted air-tight.

No mixing of the liquids is now possible; but conduction still takes place over the damp surface of the glass tube, especially if, before use, the whole bottle be slightly inclined so as to wet the edges of the tube. The slight film of zinc-salt thus formed, being hygroscopic and being in a saturated atmosphere, will keep the top of the tube sufficiently moist for an immense time.

The only possible changes which can go on in this cell are in the zinc and the solution in immediate contact with it. This solution can at any time be drawn off with a pipette and replaced by fresh, without greatly affecting the liquid in the bottle (if the cork be air-tight); and the zinc can still more easily be taken out and replaced by a new piece.

I have described the cell as at present made; but if there were any chance of its coming into use as a standard, a few modifications might be introduced. Thus the zinc might be a short rod with an india-rubber collar fitting the tube and with a short copper wire attached to it, which should project above the cork instead of the zinc, the joint being a little way down the tube and protected by a coat of varnish from damp air. A set of experiments would have to be made to determine the dependence of electromotive force on temperature; and then a thermometer with a short scale might be fixed in each cork.

University College, London.



Dotted Lines .... are Capacity Curves.
Continuous Lines ——— are Conductivity Curves.

Point A about 0·002 micro-farads capacity per cubic centimetre, temperature −12°·0 C.
Point E about 0·1185 micro-farads capacity per cubic centimetre, temperature +5° C.
Point F about 2240 megohms resistance per cubic centimetre, temperature −12°·4 C.
Point K about 0·34 megohms resistance per cubic centimetre, temperature +11°·02 C.

Ice as an Electrolyte.

W. E. Ayrton.
John Perry.

Mintern Bros. lith.

XX. *Ice as an Electrolyte.—Second Communication.* *By* W. E. Ayrton *and* John Perry, *Professors in the Imperial College of Engineering, Tokio, Japan.*

[Plate V.]

In our former paper on Ice as an Electrolyte, read before the Physical Society on May 26th of this year, we described experiments which proved, among other things, that as the temperature of ice is allowed to gradually rise the conductivity increases regularly, and that there is no sudden change in passing from the solid to the liquid state. We also determined roughly the specific inductive capacity of $\left\{\begin{matrix}\text{ice}\\ \text{water}\end{matrix}\right\}$ at −13°·5 C. and at +8°·7 C., and found that at the latter temperature it was about 2240 times as great as in the former. Preliminary experiments also showed us that there was very little change in the specific inductive capacity up to 0° C.; and it was anticipated that there would not be a very great change after 0°; we therefore concluded that a very great change must occur at the melting-point. A series of further experiments made with the same apparatus, since the writing of the previous paper, have enabled us to draw approximate curves (Pl. V.), A B C, D E for the specific capacity of $\left\{\begin{matrix}\text{ice}\\ \text{water}\end{matrix}\right\}$ from −12°·2 C. to +5° C., all tests of capacity being made by charging for ten seconds and then short-circuiting the $\left\{\begin{matrix}\text{ice}\\ \text{water}\end{matrix}\right\}$ condenser for fifteen seconds. From these it will be seen that, although the change at the melting-point is not quite as sudden as we expected, our anticipations are on the whole realized. It must be remembered too (see the description of the apparatus in our former paper) that, as the present experiments were made with a gradually rising temperature, the thermometer will always indicate a temperature a little higher than that of the ice; the curve B C ought probably, therefore, to be even more vertical than it is.

Distances measured perpendicularly to Y O Y represent temperature—positive temperature if measured to the right, and negative if measured to the left. Distances measured perpendicularly to X O X represent specific capacity per cubic centimetre for points on the dotted lines, and conductivity for points on the continuous lines. The scale for temperature is the same for all the curves. The scale for vertical distances for the capacity-curve D E is one eighth of that for the capacity-curve A B C; and the scale for vertical distances for the conductivity-curve J K is three thousandths of that for the curve F G H.

The point A corresponds with a capacity per cubic centimetre of about 0·002 microfarad, at -12 C. ; E corresponds with a capacity per cubic centimetre of about 0·1185 microfarad, at $+5^{\circ}$ C. ; at this apparent temperature the capacity was increasing so rapidly as to make exact measurements very difficult, although the temperature was increasing but slowly. The point F corresponds with a specific resistance per cubic centimetre of about 2240 megohms, at $-12^{\circ}\cdot 4$ C. ; and K with a resistance per cubic centimetre of about 0·34 megohm, at $+11^{\circ}\cdot 02$ C. As in our previous experiments, the water employed in the water-condenser was distilled, and the ice was formed by freezing it with an external freezing-mixture no particle of which was allowed to fall into the distilled water.

The important theory which Prof. Clerk Maxwell has developed, by comparing the propagation of electro-magnetic disturbances through the ether with the propagation of light-vibrations, has been illustrated only by paraffin (a non-conductor); and he has not considered the propagation of electro-magnetic disturbances in a conducting medium. But according to a former paper of ours, on the "Viscosity of Dielectrics," no dielectric can be assumed to be non-conducting, and the charging of any condenser whatever is always accompanied with absorption phenomena; also absorption certainly increases with conductivity.

Hence although, if a method of experimenting were employed in which a water-condenser of great internal resistance were discharged through wires of less and less resistance for shorter and shorter periods of time, the measured specific inductive capacity might get less and less, and gradually approach a value equal to the square of the index of refraction of water for infinitely long luminous waves (the index of refraction for air being called unity), still practically the measured specific inductive capacity can never be even approximately equal to the refractive index of water, since the absorbed charge is immeasurably greater than the surface-charge. We therefore need not expect to find the specific inductive capacity of water in its variations with temperature consistent with Dr. Gladstone's results for index of refraction. When Prof. Clerk Maxwell takes into account conductivity, his equations are not generally integrable; but even if they were they could not deal with the real case, because he leaves absorption quite out of account.

July 30, 1877.

XXI. *On a Method of measuring the Absolute Thermal Conductivity of Crystals and other rare Substances.*—Part I. *By* OLIVER J. LODGE, *D.Sc.*[*]

1. WHEN only a small portion of a substance is obtainable on which to experiment, the measure of conductivity by any dia-calorimetric method becomes difficult; and accordingly observers have contented themselves, in the case of the rarer crystalline bodies, with comparing their conductivities in different directions by Sénarmont's or some similar method. If the substance is sufficiently plentiful to be obtained in slabs (like rocks), then some modification of Fourier's "thermomètre de contact" will give its conductivity, though there are many objections to the use of this instrument.

But there is another method of Fourier's, applicable only to long rods, put in practice by Biot, Despretz, Forbes, and recently by Wiedemann and Franz (commonly known as Forbes's method), which it seems possible to modify so as to make it applicable to short rods or even slices[†]. This well-known method consists in observing the permanent curve of temperature along a cylindrical rod of the given material, one end of which is heated and the rest exposed to the atmosphere. Let s be the area of cross section (which need not be circular) and P the perimeter of the rod, the latter being defined as the length of a string wrapped once round the rod if the actual perimeter is any *re-entrant* curve. The condition to be expressed is that the total gain of heat of any element of the rod by its anterior, posterior, and exterior surfaces is equal to nothing. Taking t as the excess of temperature over that of the air of an element in a position x along the rod, we have the quantity of heat

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[*] Read January 19, 1878.

[†] The method occurred to me when thinking how best to measure the conductivity of tourmaline in opposite directions along the axis, a subject which I was considering in conjunction with Mr. S. P. Thompson of Bristol; for we had reason to think that tourmaline and all other pyro-electric crystals must necessarily possess a unilateral conductivity along their axis both for heat and electricity; and this supposition has been partially confirmed, in the case of heat, by some preliminary experiments of Mr. Thompson's last summer on a very small crystal. No further con-

$-ks\dfrac{dt}{dx}$ entering at its anterior or hotter surface in unit time,

$+ks\left(\dfrac{dt}{dx}+\dfrac{d^2t}{dx^2}dx\right)$ at its posterior surface,

$-\mathrm{P}ht\,dx$ at the surface exposed to the air ;

k being the conductivity of the rod, and h the radiation-coefficient of its surface, *i. e.* the quantity of heat lost in unit time by unit surface when it is one degree hotter than the air.

Putting the sum of these quantities equal to zero, we have

$$\frac{d^2t}{dx^2}=\frac{\mathrm{P}h}{sk}t=p^2t \text{ say,}$$

an equation whose complete integral is

$$t=\mathrm{C}_1e^{px}+\mathrm{C}_2e^{-px},$$

or, as I shall prefer to write it,

$$t=\mathrm{A}\cosh px-\mathrm{B}\sinh px.$$

The constants A and B are determined in terms of p as soon as one knows the temperatures of any two points of the rod ; and the temperature of a third point will determine p, whence, if h be separately found, k is known. Thus, suppose we know t_0 the temperature of the origin, and t_x the temperature of a

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firmation or modification of the experiment, however, has yet been possible, owing to the scarcity of the crystal and the difficulty of obtaining a large slice; but this difficulty has now been removed by the kindness of Professor Nevil Story Maskelyne.

point at a distance x from it, and also $t_{\frac{1}{2}}$ the temperature halfway between these points; then

$$A = t_0,$$

$$B = t_0 \coth px - t_x \operatorname{cosech} px,$$

$$p = \frac{1}{x} \cosh^{-1} \frac{t_0 + t_x}{2t_{\frac{1}{2}}}.$$

2. Now suppose the rod to be cut in half and a slice of crystal or any substance interposed: the curve of temperature will have a discontinuity at the junctions; but if the curve along each rod is observed, it may be possible to calculate it for the crystal. The method which I propose, then, is to cut a cylindrical piece of the substance to be examined, of length z, with flat faces, and to squeeze it between two copper or iron rods (or any other metal whose conductivity is well known) of exactly the same cross section as itself both in shape and size, putting a pad of a few thicknesses of tinfoil between the surfaces, so as to make better contact, and then to observe the curve of temperature down each rod when one end of one is heated and the further end of the other is cooled, the whole having been left long enough to attain a permanent state.

Conduction through a cylinder inserted between a pair of metal rods.

3. Let the cylinder be of length z,

and conductivity χ,

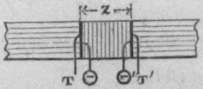
and let its surface have the radiation-coefficient h'.

Let the packing on each side be of thickness y,

and conductivity κ,

and let it be so thin that radiation from its edge is negligible.

Fig. 1.



Also let us take the atmospheric temperature as an artificial zero; so that by "temperature" we shall always mean *excess of temperature* above that of the air.

And let T and Θ be the temperatures of metal and cylinder
on each side of first packing (see fig. 1),
T′ and Θ′ ditto on each side of second packing.

Then the quantity of heat which leaves the first rod traverses the first packing and enters the cylinder, which is expressed analytically thus (k being the conductivity of the metal),

$$k\frac{d\mathrm{T}}{dx}=\kappa\frac{\Theta-\mathrm{T}}{y}=\chi\frac{d\Theta}{dx}\,; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and similarly for the quantity which crosses the second packing,

$$k\frac{d\mathrm{T}'}{dx}=\kappa\frac{\mathrm{T}'-\Theta'}{y}=\chi\frac{d\Theta'}{dx},\text{—} \quad . \quad . \quad . \quad (2)$$

four equations from which the unknown quantities, $\frac{\kappa}{y}$, Θ, and Θ′ can be eliminated, and χ be found.

Now the curve of temperature down the cylinder is, from § 1,

$$\theta=\Theta\cosh qx-(\Theta\coth qz-\Theta'\operatorname{cosech} qz)\sinh qx, \ . \ (3)$$

where

$$q^2=\frac{\mathrm{P}h'}{s\chi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

hence

$$\frac{d\Theta}{dx}=q\,(\Theta'\operatorname{cosech} qz-\Theta\coth qz)$$

and

$$\frac{d\Theta'}{dx}=q\,(\Theta'\coth qz-\Theta\operatorname{cosech} bz).$$

Substituting these values in equations (1) and (2) and eliminating, we get from the first and second of each set

$$\Theta\frac{d\mathrm{T}'}{dx}+\Theta'\frac{d\mathrm{T}}{dx}=\mathrm{T}\frac{d\mathrm{T}'}{dx}+\mathrm{T}'\frac{d\mathrm{T}}{dx}=\frac{d}{dx}(\mathrm{TT}')\,;$$

also from the first and third of each set,

$$\Theta=\frac{k}{\chi q}\left(\frac{d\mathrm{T}'}{dx}\operatorname{cosech} qz-\frac{d\mathrm{T}}{dx}\coth qz\right),$$

$$\Theta'=\frac{k}{\chi q}\left(\frac{d\mathrm{T}'}{dx}\coth qz-\frac{d\mathrm{T}}{dx}\operatorname{cosech} qz\right).$$

Therefore, combining all these,

$$\frac{\chi q}{k}\sinh qz=\frac{\left(\frac{d\mathrm{T}'}{dx}\right)^2-\left(\frac{d\mathrm{T}}{dx}\right)^2}{\frac{d}{dx}(\mathrm{TT}')}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence χ is determined in terms of q, which itself contains it together with the radiation-coefficient h' (which must be supposed known). We may write the last equation thus, by (4),

$$\frac{\sinh qz}{q} = \frac{sk}{\mathrm{P}h'} \cdot \frac{\left(\frac{d\mathrm{T}'}{dx}\right)^2 - \left(\frac{d\mathrm{T}}{dx}\right)^2}{\mathrm{T}\frac{d\mathrm{T}'}{dx} + \mathrm{T}'\frac{d\mathrm{T}}{dx}}, \quad . \quad . \quad . \quad . \quad (6)$$

which shows that this method is not satisfactory for determining q when the product qz is very small.

4. Now there are three special cases, depending on the value of h':—

(1) When the crystal has its natural surface, and the value of h' is determined by special experiment on its rate of cooling. In this case the above equation remains as written, and may be treated, as qz will generally be less than unity, by expanding the left-hand member,

$$z\left(1 + \frac{q^2z^2}{\underline{|3}} + \frac{q^4z^4}{\underline{|5}} + \ldots\right),$$

and then solving for q by successive approximations.

(2) When the crystal and rods are covered over with a coat of varnish (as Brunswick black), so that h is the same for all. In this case the coefficient of the right-hand member becomes simply $\frac{1}{p^2}$, but the treatment required is the same as in the first case.

(3) When the crystal is surrounded with cotton-wool or felt, or in some other way has its exterior surface made adiabatic, so that $h'=0$. In this case the left-hand member of the above equation equals z, and the right-hand becomes indeterminate, so that a fresh investigation is necessary.

Case when radiation from the exterior surface of the cylinder is prevented.

5. Heat will now flow through the cylinder as through part of an infinite wall, and $\frac{d\theta}{dx}$ becomes simply $\frac{\Theta'-\Theta}{z}$; hence the two sets of equations (1) and (2) are now all equal to one

another, and they reduce to

$$k\frac{d\mathrm{T}}{dx}=\kappa\frac{\Theta-\mathrm{T}}{y}=\chi\frac{\Theta'-\Theta}{z}=\kappa\frac{\mathrm{T}'-\Theta'}{y}. \quad . \quad . \quad . \quad (7)$$

But as these are only three equations between four unknown quantities, some further observation is necessary before we can determine χ. We may either omit the crystal altogether, or, what is probably better, replace it by a piece of the same metal as the rods are made of, and repeat the temperature-determinations, the packing being kept exactly the same as before. Denoting the temperatures in this case by small letters, the equations will now be

$$k\frac{dt}{dx}=\kappa\left(\frac{\theta-t}{y}\right)=k\frac{\theta'-\theta}{z'}=\kappa\left(\frac{t'-\theta'}{y}\right), \quad . \quad . \quad . \quad (8)$$

where z' is the thickness of the bit of metal. By these three equations $\frac{\kappa}{y}$ is determined; and its value may then be substituted in the former set.

Eliminating Θ and Θ' from the former set (7), we have

$$\left(\frac{zk}{\chi}+\frac{2yk}{\kappa}\right)\frac{d\mathrm{T}}{dx}=\mathrm{T}'-\mathrm{T}; \quad . \quad . \quad . \quad . \quad (9)$$

similarly from (8) we get

$$\left(\frac{z'k}{k}+\frac{2yk}{\kappa}\right)\frac{dt}{dx}=t'-t,$$

whence, getting rid of $\frac{\kappa}{y}$, we have

$$z\frac{k}{\chi}=z'+\frac{\mathrm{T}'-\mathrm{T}}{\frac{d\mathrm{T}}{dx}}-\frac{t'-t}{\frac{dt}{dx}}; \quad . \quad . \quad . \quad (10)$$

so χ is determined by the two observations.

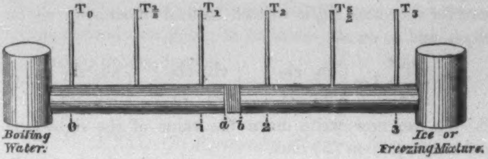
6. Although this method requires two experiments while the other (§ 3) required only one, yet it will probably be more useful than the other, as it is applicable to very thin slices of crystals—in fact the thinner the better,—whereas the other one applies more to substances in the form of a short rod; for it fails when z becomes very small. This failure of the § 3 method is due to the fact that it depends entirely on radiation going on from the cylinder at the same intrinsic rate as from the rods,

and on some appreciable quantity of heat being lost in this way during its passage through the cylinder; hence of course a certain *length* of the cylinder is essential.

Observation of the Curves of Temperature.

7. We have seen (§ 1) that, to determine the curves of temperature, it is necessary to know the actual temperature of two, or perhaps one should rather say three, points on each rod. Each rod then should have three holes bored to receive the bulb of a thermometer, one near each end, at a distance l from one another, and another in the middle halfway between the other two. Let the temperatures which these thermometers indicate above that of the air at the time be denoted by T_0, $T_{\frac{1}{2}}$, T_1, T_2, $T_{\frac{5}{2}}$, T_3, their position being shown in the figure.

Fig. 2.



Denote the distances thus:—

$$0\,a = l_0 = b\,3,$$
$$1\,a = l_1 = b\,2,$$
$$0\,1 = l = 2\,3 = l_0 - l_1;$$

then measuring x from 0 for the first rod, we have as the curve of temperature down it, by § 1,

$$t = \mathrm{A} \cosh px - \mathrm{B} \sinh px;$$

that is,

$$t = \mathrm{T}_0 \cosh px - (\mathrm{T}_0 \coth pl - \mathrm{T}_1 \operatorname{cosech} pl) \sinh px \; ; \quad . \quad (11)$$

similarly down the second rod, reckoning x from b, the curve is

$$\left.\begin{aligned} t' &= \mathrm{A}' \cosh px - \mathrm{B}' \sinh px, \\ \text{where} \quad \mathrm{A}' &= \frac{\mathrm{T}_2 \sinh pl_0 - \mathrm{T}_3 \sinh pl_1}{\sinh pl}, \\ \text{and} \quad \mathrm{B}' &= \frac{\mathrm{T}_2 \cosh pl_0 - \mathrm{T}_3 \cosh pl_1}{\sinh pl}. \end{aligned}\right\} \quad . \quad . \quad . \quad (12)$$

We can now at once express the values of the "known quantities" which occur in equations (1) and (2), and in the right-hand members of equations (5) and (6), viz.

$$\mathrm{T}, \quad \mathrm{T}', \quad \frac{d\mathrm{T}}{dx}, \text{ and } \frac{d\mathrm{T}'}{dx}.$$

Thus

$$\left.\begin{aligned} \mathrm{T} &= \frac{\mathrm{T}_1 \sinh pl_0 - \mathrm{T}_0 \sinh pl_1}{\sinh pl}, \\ \frac{d\mathrm{T}}{dx} = \left(\frac{dt}{dx}\right)_{x=l} &= p\,\frac{\mathrm{T}_1 \cosh pl_0 - \mathrm{T}_0 \cosh pl_1}{\sinh pl}, \\ \mathrm{T}' = \mathrm{A}' &= \frac{\mathrm{T}_2 \sinh pl_0 - \mathrm{T}_3 \sinh pl_1}{\sinh pl}, \\ \frac{d\mathrm{T}'}{dx} = \left(\frac{dt'}{dx}\right)_{x=0} = -p\mathrm{B}' &= p\,\frac{\mathrm{T}_3 \cosh pl_1 - \mathrm{T}_2 \cosh pl_0}{\sinh pl}. \end{aligned}\right\} \quad (13)$$

The symmetry of these expressions is visible in the following, where for shortness sh_0 is written instead of $\sinh pl_0$, ch_1 for $\cosh pl_1$, and so on :—

$$\mathrm{T} : \frac{d\mathrm{T}}{pdx} : 1 = \begin{vmatrix} \mathrm{sh}_0 & \mathrm{sh}_1 \\ \mathrm{T}_0 & \mathrm{T}_1 \end{vmatrix} : \begin{vmatrix} \mathrm{ch}_0 & \mathrm{ch}_1 \\ \mathrm{T}_0 & \mathrm{T}_1 \end{vmatrix} : \begin{vmatrix} \mathrm{sh}_0 & \mathrm{sh}_1 \\ \mathrm{ch}_0 & \mathrm{ch}_1 \end{vmatrix} \quad (14)$$

8. We can now write down the value of the right-hand member of equation (5) thus,

$$\frac{\left(\frac{d\mathrm{T}'}{dx}\right)^2 - \left(\frac{d\mathrm{T}}{dx}\right)^2}{\mathrm{T}\frac{d\mathrm{T}'}{dx} + \mathrm{T}'\frac{d\mathrm{T}}{dx}} = \frac{p^2\{(\mathrm{T}_3\,\mathrm{ch}_1 - \mathrm{T}_2\,\mathrm{ch}_0)^2 - (\mathrm{T}_1\,\mathrm{ch}_0 - \mathrm{T}_0\,\mathrm{ch}_1)^2\}}{p(\mathrm{T}_1\mathrm{T}_3 - \mathrm{T}_0\mathrm{T}_2)\sinh pl}; \quad (15)$$

so (6) becomes

$$\frac{\sinh qz}{q} = \frac{h}{h'} \cdot \frac{\{(\mathrm{T}_0 + \mathrm{T}_3)\cosh pl_1 - (\mathrm{T}_1 + \mathrm{T}_2)\cosh pl_0\}\,\{(\mathrm{T}_0 - \mathrm{T}_3)\cosh pl_1 - (\mathrm{T}_1 - \mathrm{T}_2)\cosh pl_0\}}{(\mathrm{T}_0\mathrm{T}_2 - \mathrm{T}_1\mathrm{T}_3)\sinh pl}, \quad (16)$$

which is a form convenient for calculation.

9. So also for the second method (§ 5), we can write down the value of the quantities occurring in the right hand of (10),

$$\frac{\mathrm{T}' - \mathrm{T}}{\frac{d\mathrm{T}}{dx}} = \frac{(\mathrm{T}_1 - \mathrm{T}_2)\sinh pl_0 - (\mathrm{T}_0 - \mathrm{T}_3)\sinh pl_1}{p(\mathrm{T}_0\cosh pl_1 - \mathrm{T}_1\cosh pl_0)}; \quad (17)$$

and similarly for the small t's, of which a set t_0, t_1, t_2, t_3 have been observed. In this case there is no loss of heat in passing through the crystal; so we ought to have

$$\frac{d\mathrm{T}}{dx}=\frac{d\mathrm{T}'}{dx},$$

which gives the condition

$$\frac{\mathrm{T}_1+\mathrm{T}_2}{\mathrm{T}_0+\mathrm{T}_3}=\frac{\cosh pl_1}{\cosh pl_0}; \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and unless this condition is satisfied there is some error in the experiment, and it is useless to proceed.

I have to express my thanks to my brother, Mr. Alfred Lodge, of St. John's College, Oxford, for several suggestions in the writing out of the above and for some improvements in the notation.

In the second part of this communication some practical details will be given, together with the results of some trials of the method now going to be made.

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XXII. *On Permanent Plateau's Films.*

By SILVANUS P. THOMPSON, *B.Sc. B.A.*[*]

1. THE film-figures, which occupy so large a part of the researches of Plateau[†] upon the Molecular Statics of Liquids, when prepared with the glyceric fluid prescribed by their discoverer, are of extreme fragility and of short duration. With such a liquid films have been made which lasted ten, twelve, or even sixteen hours in the air, and from fifteen to thirty hours when protected by an external vessel of glass. In one instance[‡], where chloride of calcium had been added to the liquid, a duration exceeding fifty-four hours was observed. The average duration of the films, especially if they are to be exhibited to a number of persons, is more brief.

No method hitherto described of producing these films in a more durable or permanent form has been quite satisfactory, though there have been several attempts. Of these the writer was not aware when he began the present investigation, though most of them are mentioned in the later chapters of Plateau's work already named. A brief enumeration of these attempts will therefore preface a description of the process now announced for rendering the films permanent.

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[*] Read December 15, 1877.

[†] *Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires.* Par J. Plateau. Gand et Leipzic: 1873

[‡] Plateau, *op. cit.* vol. i. p. 175, § 106.

2. M. Plateau has himself endeavoured* to fix the film-figures by dipping the wire frames into solutions which evaporate, leaving films of greater or less tenacity. He was unsuccessful with collodion and with albumen. A solution of gutta-percha in bisulphide of carbon gave better results. The system of films upon a cubical frame of 2 centims. side was preserved for several months, but eventually fell to powder. The same substance refused to form a film upon a frame of 3 centims. side. Glass, which in the single instance of the spherical film or bulb is so familiar, presents too many difficulties to be applicable for the production of the film-figures.

Schwartz† succeeded with much ingenuity in obtaining the anticlastic film-surface upon a skew quadrilateral frame whose sides were 3·5 centims. long, with gelatine.

Prof. Mach‡ imitated the system of films developed upon a tetrahedral frame with thin laminæ of caoutchouc covering the sides, and drawn together when the air was exhausted from within.

Better results have been yielded by viscous liquids which solidify at temperatures moderately low.

M. Rottier, of Ghent, has obtained films of considerable dimensions with a mixture, suggested by Böttger in 1838 for blowing bubbles, consisting of 8 parts of resin (colophony) with 1 of linseed oil, and fusing at 97°. But the films were always found after a few hours to have broken by contraction.

Mach§ has obtained films upon a tetrahedral frame of 5 centims. side dipped in fused resin. He has also obtained films from solutions of alkaline silicates which hardened on exposure to the air.

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* Plateau, *op. cit.* vol. ii. p. 119, § 311.

† Ibid. vol. i. p. 233, § 141.

‡ *Die Gestalten der Flussigkeiten.* Prag.: 1872. See also Plateau, *op. cit.* vol. ii. p. 374, § 210 *bis.*

§ *Wiener akademischer Anzeiger,* 1862, vol. xlvi. 2nd part, p. 125, "Ueber die Molecularwirkung der Flussigkeiten."

M. Plateau* has found a mixture of 5 parts of resin with 1 part of gutta-percha superior to resin alone. A system of films upon a cubical frame of 5 centims. side, prepared by M. Donny, was preserved for two years, but ultimately fell into fragments.

3. The author's first experiments were made with pure amber-coloured resin fused. The resulting films were brittle and of irregular thickness. When 10 per cent. of turpentine was added, the liquid was too mobile at high temperatures to form films, and at low temperatures too stiff to form them regularly.

A mixture of pure resin with Canada balsam was tried, with good results; and a series of experiments followed, to ascertain the best proportions. When the mixture contained a less proportion of balsam than 35 per cent. the films were too brittle, and irregular in form. If it contained more than 70 per cent. of balsam the films did not readily harden, and were not formed without difficulty. A mixture of 55 per cent. of resin with 45 of balsam, which fused about 85°, gave good films, tough on cooling, but somewhat brittle. The mixture yielding the most satisfactory results contained 46 per cent. of resin and 54 of balsam. This mixture is sufficiently fused at 80° to be workable, but yields the best films at 93° to 95°. At 105° films can be obtained; and they are thinner than those formed from the more viscid fluid at 95°. At 110° films are still obtainable; and they frequently exhibit chromatic phenomena, but usually burst before hardening.

[The specimens exhibited to the Society are made with this mixture. They include a cubical frame of 2·5 centims. side, and a tetrahedral frame of 3·1 centims. side. Larger specimens have been obtained, however, though they generally show some imperfection of form. I have had a flat circular frame of 11 centims. diameter covered with a film of beautiful transparency. Brass wire appears better than iron for the frames.]

The films made with the mixture described are remarkably tough, and if preserved from rough handling appear to be of indefinite durability. A number of frames holding films have been hanging for over two months unprotected upon the wall of the laboratory of the writer, and are still intact. Brass wire of 0·33 millim. in diameter has been employed for the construction of the frames. When a thicker wire is used, the films become irregular from the longer retention of heat by the wire, and the consequent earlier cooling of the central portions of the films.

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* *Op. cit.* vol. ii. p. 119, § 314.

As with the soap-films, so with those of resinous matter, success depends largely upon the purity of material employed. Dust and oily matters must be scrupulously excluded; and the resin should be retained at a temperature near its boiling-point for some time, to purify it of more volatile matter, before the balsam is mixed with it.

The most perfect films are obtained when the wire frames, after being dipped in the liquid, are removed to an air-bath at the temperature of about 80°, in which they are left, and the whole is allowed slowly to cool.

In proof of the toughness of the films, it may be mentioned that a recent flat film upon a circular frame of 4 centim. diameter of iron wire of 0·9 millim. gauge sustained, without breaking, the pressure of a cylindrical fifty-gramme weight, of 24 millims. diameter, placed upon its centre.

XXIII. *On Grove's Gas-Battery.*

By HENRY FOSTER MORLEY, *M.A.*, *B.Sc.*[*]

IT appears to me that the question as to the mode of action of the well-known gas-battery has not yet been definitely settled.

1. The discoverer says, "The chemical or catalytic action can only be supposed to take place, with ordinary platina-foil, at the line or water-mark where the liquid, gas, and platina meet"[†]. Nevertheless he showed that water containing oxygen in one tube and hydrogen gas in the other tube gave a conti-

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[*] Read March 16, 1878.

[†] Phil. Mag. December 1842. See also Phil. Trans. 1843, p. 107.

nuous current*. As regards exp. 29 in the last-quoted excellent paper (viz. the experiment in which, hydrogen being in one tube and nitrogen in the other and no oxygen being dissolved in the liquid, hydrogen was found to appear in the nitrogen tube), as Mr. Grove does not say that there is a current, and as the presence of a current would contradict the conservation of energy, I am inclined to think that the effect is due to diffusion, and that it would occur whether the platinums were joined or not.

2. Mr. Justice Grove says that the phenomenon does not take place when the nitrogen is absent and its place filled by the liquid; and this is just what we should expect if the effect is due to diffusion. Mr. Grove thought it just possible that the hydrogen decomposed the water in its tube, combining with the oxygen, and that an equal amount of hydrogen was liberated in the other tube. Since the total amount of water is not changed, it is clear that such a decomposition could not be accompanied by a current.

3. Nevertheless Dr. Schönbein said that pure water containing no oxygen in one tube and an aqueous solution of hydrogen in the other gave a continuous current†. M. Gaugain makes the same assertion, but adds that he deprived his water of air by boiling‡. To boil water and then let it stand in the air is evidently not enough to deprive it of oxygen; hence these anomalous results may be due to the water not having been absolutely free from oxygen. Such a current, as before stated, would contradict conservation of energy: indeed it has been shown by Mr. Grove that water absolutely free from oxygen in one tube and hydrogen gas in the other tube produces no current§.

4. In one experiment Mr. Grove arranged his platinum plates, which I believe were platinized, in such a way as just to cut the surface of the liquid in the tubes: he got a strong current until the liquid rose above the platinum, when it became very weak. M. Gaugain says, and, I think, rightly, that this is due to the greater thickness of liquid through which the

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[*] Phil. Trans. 1843, exp. 28 &c.

[†] Phil. Mag. March 1843.

[‡] *Comptes Rendus*, February 25, 1867; Phil. Mag. June 1867.

[§] Phil. Trans. 1843, exp. 7 and elsewhere.

gas must now pass in order to get at the platinum—when the platinum is partly exposed the film along the line of junction being extremely thin.

5. M. Gaugain made a cell in which the platinum plates were movable, and determined, by the method of opposition, the electromotive force when the plates were partly exposed; he then lowered them until they were wholly immersed, and determined the electromotive force immediately. In this experiment the current was only allowed to flow for a few seconds. He found that the two determinations were the same, and concluded that the action of the battery depends entirely upon dissolved gas. It is, however, open to any one to assert that the platinums, when lowered, retained minute bubbles of gas on their surface, and that thus there were still many points of contact of liquid, gas, and platinum.

6. M. Gaugain, following Dr. Schönbein, asserts that "the oxygen serves simply to depolarize the positive wire," and "that its function is that of sulphate of copper in Daniell's cell"—in other words, that, were it not for the opposition current developed by the freshly-deposited hydrogen, the current could be kept up indefinitely without the presence of oxygen. As I have before stated, I cannot conceive this state of things.

I. In order to show that some, at all events, of the current in the gas-battery is due to dissolved gases, I made the following experiments in the laboratory of Professor Carey Foster:—A gas-couple with wholly submerged non-platinized platinum plates was charged by electrolysis and short-circuited for a week, after which the lengths of the columns of oxygen and hydrogen were read off by means of a telescope on different days, the couple being all the while short-circuited. A similar couple, from which the platinum plates were removed after it had been charged, was similarly treated.

The barometer-reading was, of course, corrected for expansion, for the column of liquid below the gas, and for aqueous tension, the slight effect of sulphuric acid on the aqueous tension being neglected. A correction was applied for the curved ends of the tubes, and the corrected lengths reduced to 0° C. 760 millims.

The result in millimetres for the couple without platinum plates was:—

	Nov. 13.	Dec. 11.	Jan. 9.
Hydrogen	76·3	76·4	76·3
Oxygen	49·9	49·7	49·7

Practically the volume of the gas in these tubes was not altered by diffusion.

For the tubes which contained the platinum plates the lengths were:—

	Nov. 13.	Nov. 20.	Dec. 11.	Jan 9.
Hydrogen	56·5	56·6	55·5	55·0
„ calculated	56·6	56·4	55·75	54·9
Oxygen	...	34·4	34·2	34·2

The second line is calculated from the first by least squares, on the assumption of a uniform decrease of hydrogen. The greatest error is ¼ millim.; and 1·7 millim. has disappeared. The oxygen seems to have been supplied by the air.

II. On December 11 I joined the plates through a galvanometer of 6917 ohms resistance. The connexion through the galvanometer was made without previously breaking the circuit; yet a current was instantly shown; after 19 hours the deflection was 20½ divisions. By comparison with a Daniell's cell whose electromotive force I assumed to be 1·1, I found that a deflection of 1 division indicated a current of ·00000000056 electromagnetic unit.

If we assume that the current in the short circuit is the same as that passing through the galvanometer, an assumption which later experiments show to be not far from the truth, we shall find that 8 cubic millims. of hydrogen per week would be required to keep up this current. Now 32 cubic millims. have actually disappeared per week. The difference may be partly due to the inaccuracy of the assumption just made, and partly to the fact that some of the hydrogen combines with oxygen that has found its way from the air into the hydrogen-tube, the local currents thus produced not contributing to the main current.

III. An experiment similar to I., in which, however, the gases were prepared chemically, and in which there was also a gas-couple whose plates were not joined by a wire. The lengths of gas, in millimetres, corrected as before, were:—

For the couple with joined plates—

	May 8.	Oct. 4.	Loss.	Volume lost, in cubic centims.
Hydrogen	146·1	136·0	10·1	2·87
Oxygen	64·8	62·7	2·1	·60

For the couple with unjoined plates—

	May 8.	Oct. 4.	Loss.	Volume lost, in cubic centims.
Hydrogen	63·9	59·3	4·6	·90
Oxygen	64·1	61·3	2·8	·44

For the couple with no plates—

Hydrogen	92·0	86·9	5·1	1·30
Oxygen	90·0	85·4	4·6	·74

In this case a good deal of gas seems to have been lost by diffusion.

The ratio of hydrogen lost to oxygen lost in the three cases is 4·8, 2·1, and 1·8 respectively. If we assume that 1·8 is the ratio of the gases lost through diffusion, and that the loss of oxygen in the first two cases is due solely to this cause, we shall find that 1·79 and ·11 cubic centim. of hydrogen respectively still remain to be accounted for in the two cases. I attribute this loss to local currents in the second case, and partly to these but chiefly to the main current in the first case, most of the necessary oxygen being supplied by the air to the liquid.

IV. If the hydrogen in a gas-couple with submerged plates be warmed by the hand, the current is increased; and if it be cooled the current is diminished: indeed it is very sensitive to changes of temperature, and of pressure also; and hence it is hardly possible to determine its strength with much accuracy. The further any horizontal layer of liquid in the hydrogen-tube is from the gas, the less hydrogen does it contain. Any expansion of the gas from heat or decrease of pressure brings a more saturated solution into contact with the immersed plate and the current increases, whereas contraction produces the opposite effect.

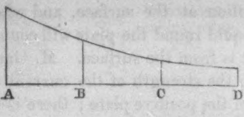
V. When a cell has been recently charged by electrolysis the current is at first very strong; but it soon falls off, and at last remains of nearly constant strength. This is because the water was at first saturated with the gas, but this gas being used up by the current takes some time to be restored by solution at the surface, and when equilibrium is attained the liquid round the plate will contain less dissolved gas the further it is from the surface. M. Gaugain attributed the falling-off in the strength of the current to the deposition of hydrogen on the positive plate; there is no need, however, for any such supposition. I employed a battery in which the plates were wholly immersed; and the final current varied with the depth of the top of the plate in the hydrogen-tube from the surface, and with the resistance in circuit, as the following Table shows:—

n.	C.	R.	E.	C calc.
63	25	240,000	6,000	25
63	39	11,600	450	40
63	42	1,600	67	41
8	203	10,200	2,070	204
7·5	217	200	43	219
10·5	201	10,200	2,050	196
11	81	244,500	19,800	81
0	277	10,200	2,800	224
0	91	234,500	21,300	89

n is the distance between top of plate in hydrogen-tube and surface of liquid in that tube, in millimetres; $n=0$ means that the plate cuts the surface and rises about 1 millim. above it: the plate in the oxygen tube was always at the same distance from the surface and was wholly immersed. C is the final strength of current, usually several hours after introducing resistance, given in deflections of the galvanometer, each of which is about ·00000073 weber. R is the resistance in ohms; and E is $\frac{CR}{1000}$.

In the first place, it seems that the increase of current consequent on causing the platinum to cut the surface is too slight to oblige us to assume that a new force is thereby brought into action; in other words, the whole of the current in the gas-battery is due to dissolved gas.

I tried to express the relation between *n*, C, and E in a formula obtained theoretically. In this I had but little success; but perhaps I may venture briefly to indicate the results:—



Let abscissæ represent depth below surface; ordinates quantity of hydrogen in solution at any level, supposed uniform. Imagine a tube of uniform bore open to air at D and to hydrogen at A. Suppose B C a uniform platinum rod, or rather an indefinite number of infinitely near equal platinum plates. Consider them to form equal branches of a divided circuit, and suppose the strength of current the same in each.

Suppose the number of molecules of hydrogen ejected from any layer in a given time to be proportional to the total number in that layer. Let u_x be the quantity of hydrogen in a layer at distance x from A; then, when equilibrium is attained, $\Delta^2 u_{x-1}$ is proportional to the number of molecules destroyed in that layer in a given time; hence it is 0 between A and B and between C and D, but it is constant between B and C; or the curve representing quantity of hydrogen is straight, except between B and C, where it is conic. I assumed that there is no discontinuity, and that the electromotive force is proportional to the mean quantity of hydrogen in any layer between B and C, or, what is the same thing, to the total quantity between those limits, and that the current is proportional to the total quantity destroyed per second. Hence I deduced the formula

$$(1+na)\mathrm{C}=b-(c+nd)\mathrm{E};$$

where a, b, c, d are constants depending on the lengths BC, CD, on the rate of escape of gas at D &c. The layer A was assumed to be always saturated. In the actual experiment the shape of the plates was by no means regular; and even had they been quite regular, the assumption that the whole of each horizontal layer is a uniform solution is far from the truth. So I wrote the formula in a little more general form,

$$(1+na)\mathrm{C}=b+ne-(c+nd)\mathrm{E}.$$

If in this we put $a=\cdot0006$, $b=244\cdot5$, $e=-3\cdot2$, $c=\cdot00725$, $d=-\cdot0000715$, we get the last column (called "C calc.") given above. We should expect the last two results to be higher than the calculated values, since no allowance has been made for the capillary film rising round the emerging platinum. However, the formula evidently cannot hold for depths much greater than 63, and it would become necessary to introduce terms varying as n^2 &c.

VI. From the above Table it is clear that the electromotive force is not constant, as in ordinary voltaic cells, but rises with the resistance. The same thing happens with ordinary gas-couples with platinized platinum. In one case, changing the external resistance from 46 to 10,000 only lowered the current from 423 to 157; in another case, changing resistance from 10,000 to 190,000 lowered the current from 690 to 140.

When the resistance is suddenly increased the strength of current suddenly falls, but it rises, at first quickly and afterwards more slowly, to near its former value. For when the resistance is increased the current falls by Ohm's law; but it now uses up less gas, so that the gas accumulates in the liquid, and by so doing raises the electromotive force, and therefore the current; and this continues until equilibrium is attained.

So when the resistance in circuit is diminished the current rises suddenly, but afterwards falls to near its former value. For the current rises by Ohm's law; but the increased current uses up more gas, and so impoverishes the liquid surrounding the platinum, thereby diminishing the electromotive force, and the current falls.

These observations seem fatal to the hypothesis that the action occurs at the junction of liquid, gas, and platinum; for the gas at that point remains of constant density, whatever the resistance in circuit may be.

VII. As an example of these views, an ordinary gas element with platinized plates was joined through a resistance of about 10 ohms, including a galvanometer. After about 1½ hour the galvanometer was deflected 195 divisions; and after 19 hours the deflection was 189. The gas-element was now slanted at an angle of 40°, the plates forming inclined planes; the current rose gradually, and after 2½ hours the deflection was 235, after 23½ hours it was 221. The element was now rotated 90°, so that the plates were vertical, but their long diameter was still inclined at 40° to the horizon; the current rose instantly to 265, and after 4½ hours the deflection was 262.

When the plates form inclined planes the line of junction between liquid, gas, and platinum is not altered; but the whole surface of the liquid is increased, and the submerged plate is brought nearer to it; hence the current is increased. In the last position an increased line of junction is added, and the current is still greater.

VIII. The current produced by the ordinary gas elements which I used was always greater when the tubes contained but little gas than when they were full of gas, the ratio being, in three cases, 1¾, 7, and 18. This is because the greater the distance between the surface of the liquid in the tubes and the air the purer will the solution of gas near that surface be. Perhaps also the greater length of the plate may enable it to catch gas that would otherwise escape: the internal resistance between the most active parts, those near the surface, would be rather increased than diminished.

However, the cells are not at all regular in their action; and this may be due to irregularities in the deposition of the finely divided platinum on the plates. These irregularities do not affect VII., since the tendency of the cell on that occasion was to become gradually weaker.

IX. M. Gaugain found that the electromotive force of platinum-wire electrodes partly exposed to the gas was not altered by submerging them. I have said why this does not appear to me conclusive (5). But I inverted the experiment: ignited wires were put several centimetres below the surface of the gases; the electromotive force was 102. They were then raised so as to be only just submerged; the force was 134. They were then thrust up into the gases, and the force was 136. A key connecting the wires through a galvanometer was pressed down until the needle had got to the end of its first swing; when the needle had come to rest the operation was repeated; and the mean of the two swings is the number given above. The result agrees with M. Gaugain's experiment.

X. On another occasion I measured the electromotive force of wholly submerged wires in a gas-couple by connecting them to a condenser, and afterwards discharging the condenser through a galvanometer. The electromotive force of thick and thin platinum wires was the same; but this was 15 times that of a wire of gold. Probably in the gas-couple, as elsewhere, platinum exerts some specific attraction on hydrogen.

XI. M. Gaugain considers the falling-off in the strength of a gas-couple after short-circuiting to be due to the deposition of hydrogen on the positive wire, which hydrogen is produced by the decomposition of water by hydrogen; and he says that when the electromotive force of a couple fell from 152 to 30, that of the hydrogen-wire fell 26, while an antagonistic force of 96 was developed by the wire in oxygen*. From other experiments of M. Gaugain, I infer that the potential of each wire was compared with that of a third wire plunged in the liquid between the two tubes of the couple. He does not distinctly say that the positive wire of the couple actually became negative to the third wire, though this may perhaps be inferred from the expression "antagonistic." I consider the loss of potential to be due to the liquid near the wires becoming impoverished of gas; and even should the oxygen-wire become negative to the third wire, it may only show that the liquid in its neighbourhood contains less oxygen than that surrounding the third wire. But since a little hydrogen must have found its way into the oxygen-tube, this has a much better chance of becoming attached to the platinum when there is little oxygen near to use it up (that is, when a current is passing) than when the circuit has been broken and the wire is surrounded by a strong solution of oxygen. Using a gas-couple with wholly submerged platinum wires, and comparing these with a third wire in the liquid between the tubes by means of a condenser periodically discharged through a galvanometer, I found in two different cases, *a* and *b*, just before short-circuiting:—

	a.	*b.*
Hydrogen-wire	108	74
Oxygen-wire	12	17
	120	91

and in the same soon after breaking the circuit:—

	a.	*b.*
Hydrogen-wire	41	12
Oxygen-wire	0	12
	41	24

In one case the oxygen-wire gave a negative deflection of about 1.

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* *Comptes Rendus*, 1867.

I found that when I ignited a platinum wire in a Bunsen's flame it acquired a positive potential of about 20, as if it had absorbed oxygen. In §§ IX., X., and XI. the cell was composed of a couple of test-tubes inverted in a beaker of acid, and the wires were introduced by pushing them through a couple of narrow U-tubes, the shorter arms of which were inside the test-tubes. This arrangement made it very easy to change the wires.

XII. The maximum polarization of a voltameter is scarcely, if at all, altered by diminution of pressure (Crova); and the same seems to hold for increased pressure. So also is the electromotive force of a freshly charged gas-couple—being, in fact, little less than that maximum polarization. I connected the terminals of a gas-couple with a condenser which could be discharged through a galvanometer; I then developed gas by electrolysis for a few minutes, during which time the difference of potential between the wires, which I will call E, was 189, the pressure being 77 centims. of mercury; the battery was then cut out, and as soon as most of the bubbles, except those sticking to the wires, had risen, I found E=60. The wires were now short-circuited until E=34, when the pressure was increased to 145 centims., after which the battery was put on and E=191; then the battery was cut out as before, and E=62; then the wires were short-circuited till E=37; then the pressure was reduced to 22 centims.; then the battery was put on, and E=200; after cutting out the battery, E=60. The initial electromotive force of the element is not affected by the length of time the battery is in circuit.

The difference of potential between the terminals of the battery was about 260, but was slowly rising during the experiment. When hydrogen is liberated from the surface of the wire, the platinum attracts as much of it as it can: this quantity seems not to vary with the pressure; I do not know why it should so vary; and it determines the maximum polarization. The slight increase of the polarization with pressure may perhaps be attributed to changes in the density of the oxygen.

XIII. A gas-couple charged with chemically prepared oxygen and hydrogen was short-circuited through a galvanometer of 123 ohms resistance, and subjected to various pressures, the top of the wire in hydrogen being 5·7 centims. below the surface of the liquid in its tube, and that of the wire in oxygen being 5·4 centims. below the surface. At a pressure of 76 centims., deflection 15. At a pressure of 144 centims. the deflection gradually rose in 7 hours from 12 to 26. The hydrogen-wire being 2·1, and the oxygen wire 1·9 centim. below the surface,

at a pressure of 76 the current is 38,
" " 40 " " 20 after 6 hours,
" " 16 " " 7¼ after 5 hours.

Now pressure divided by current for the last three cases gives 2, 2, 2·2 respectively; or the current is directly as the pressure. In the last case 7¼ seems to be somewhat too low; but this may be attributed to bubbles of oxygen, which under the low pressure were given off in the hydrogen tube. For the first two cases, pressure divided by current gives 5·1 and 5·5 respectively. It is possible that at the end of the second experiment the current was very slowly rising: the further the wires are from the gas, the longer, of course, does it take for equilibrium to be attained.

In this experiment the gases were introduced by stopcocks into the upper parts of the branches of a U-tube, the platinum wires were sealed into the lower parts of those branches, and the bend of the tube had a tail by which the pressure was applied; so that the gases were introduced without coming into contact with the wires. The same instrument, being at hand, was used in § XII., where it is called a voltameter.

If the action of the gas-couple depends entirely on solution, it is natural that the current should be proportional to the solubility of the hydrogen—that is, to the pressure. But if there is really any antagonistic force kept up by hydrogen attached to the positive wire, we should expect that this force would not be altered by pressure, and so the whole current could not be proportional to the pressure. I suppose that when, by increased pressure, the electromotive force becomes equal to the maximum polarization, further increase of pressure would not alter the current.

The Physical Laboratory,
University College, London,
December 1877.

XXIV. *On some Physical Points connected with the Telephone.*

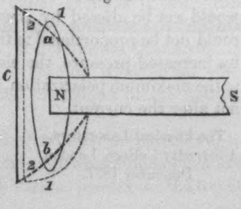
By William Henry Preece, *Vice-President of the Society of Telegraph Engineers, Memb. Inst. C.E., &c.*[*]

The introduction of the speaking telephone, by Alexander Graham Bell, has supplied physicists with an instrument of research as well as with an instrument of practical utility. It is an apparatus which, for the examination of certain kinds of currents of electricity, is the most delicate that has yet been invented. Indeed it has rendered evident the presence of currents whose existence, though suspected, have hitherto eluded the grasp of the electrician; in fact its very delicacy has proved the greatest obstacle to its general adoption.

I. *The Telephone as a Source of Electricity.*

Faraday showed that, when a closed conductor is moved across the lines of force in a magnetic field, a current of electricity is generated within that conductor whose strength is dependent upon the velocity of motion of the conductor and upon the intensity of the magnetic field. It is, in fact, proportional to the number of lines of force cut through per unit of time. And also, when lines of force are projected through a closed conductor, a current of electricity is generated in that conductor, whose strength depends upon the magnetic intensity of those lines of force, or upon their number per unit area. The direction of the current in each case is found by Lenz's law, viz. that the current produced tends to resist the motion producing it. The new principle that has been developed by Professor Graham Bell is that the form and duration of that current is dependent upon the rate and duration of the motion of the moving body or of those lines of force.

Fig. 1.



Let N S, fig. 1, be a permanent magnet, and $a\,b$ a fixed, closed, conducting ring of copper around one pole of that magnet. Let c be a movable iron armature. Now, if we regard any two lines of force 1 radiating from the pole N, and nearly cutting the ring $a\,b$, then, as we make c approach or recede from N, those lines of magnetic force will change their direction, taking up position 2; and with each change of direction they will cut the ring *a b*, and currents of electricity in different directions will circulate through *a b* according to the direction of motion of the lines of force; and the rate of increase and decrease of magnetic intensity (or of the increment and decrement of the current) will vary directly with the rate of motion of the armature *c* to or from the pole N. Thus, if *c* be a disk of iron vibrating under the influence of sound, the excursions to and fro of any point of the disk, though very small (in fact they are so small that they can scarcely be detected by the most delicate means—so small that they have led Graham Bell to imagine that the vibrations are molecular), are nevertheless sufficient to produce that motion of the lines of force which results in currents. It is, however, a fundamental principle in acoustics, that wherever there is sound there is always vibration. Sound and vibration are concomitant and inseparable phenomena. The air cannot produce sound unless it is thrown into vibration; and the air itself cannot be thrown into vibration unless the mass of matter in contact with it vibrates also. The amplitudes of vibration of the particles of the air themselves have never been measured, though the length of a sound-wave (a very different quantity) is accurately known. Lord Rayleigh has shown that an amplitude of only $\frac{1}{10000000}$ of a centimetre is sufficient to produce sonorous vibrations. But though the amplitude of the vibrations be so small they are rapid. Now this rate of motion is sufficient to bend in the same ratio the lines of force cutting *a b*, and thereby to produce currents of electricity in the ring *a b* whose number depends on the number of vibrations, and whose form and intensity depend on the rate and amplitude of motion of the disk *c*. These currents are alternate, and so rapid that no known instrument but the telephone indicates them; but they are readily shown by a Thomson's reflecting galvanometer when the disk is gently and slowly pressed in by the finger,—in one direction when the disk is pressed in, in the other direction when the disk is allowed to fly back.

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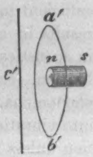
[*] Read January 19, 1878.

I have failed hitherto to make even an approximate measurement of their minuteness. We have no known standard to compare them with: we can only trust to the ear; and that instrument is not only deceptive but variable. They are certainly less than $\frac{1}{1000000}$ of an ordinary working current. Mr. R. S. Brough, of the Indian Government Telegraph Department, has calculated that the strongest current with which a telephone is at any moment worked does not exceed $\frac{1}{1000000000}$ of the C. G. S. unit, or *weber*; and Professor Pierce, of Boston, found that similar effects are produced with an electromotive force of less than $\frac{1}{200000}$ of a volt or Daniell's cell. Thus we have a source of electricity competent to produce currents of microscopic strength, which vary in form, duration, and intensity with the motion of the body producing them.

II. *The Telephone as a Detector.*

Fig. 2.



Let $n\,s$, fig. 2, be a core of soft iron surrounded by a closed conductor $a'b'$, through which currents flow. Now this core will become magnetized with an intensity dependent solely upon the intensity of the current; and the intensity of magnetism at any moment will be a function of the intensity of the current at that moment; so that if the current increase and decrease with a given ratio and at a given rate, the intensity of magnetism will increase and decrease with the same ratio and at the same rate. The disk c' is elastic, but it is rigidly fixed at its axis; it being of iron, it is attracted at any moment with a force dependent upon the intensity of the magnetism of the core $n\ s$, and being elastic, it recovers, or tends to recover, its normal position whenever this intensity of magnetism ceases or diminishes. Thus, if the magnetic intensity varies, the force of attraction varies, and the rate of motion of the disk varies in the same way. Hence the disk will record exactly the variations of the currents; and as the currents are the result of the variations of the vibrations of another disk, the one disk c' simply repeats exactly the vibrations of the other disk: thus sounds are reproduced.

Though in the earlier instruments the coil surrounded a pole-piece of soft iron, this pole-piece has since been discarded, and the coil surrounds the pole of the magnet itself. The efficacy of the instrument has been in no way impaired by this change; and it has the additional advantage of being perfectly reversible, the same instrument being used for speaking and for hearing.

III. *Working the Telephone.*

There is a remarkable difference in the power of different voices to work the telephone. Shouting is of no use. The intonation must be clear and the articulation distinct, and the style of conversation approach more the sing-song. I have heard Mr. Willmot, one of the electricians of the Post Office, through resistances that have drowned all other voices. The vowel sounds always come out the best; the palatal sounds *c*, *g*, *j*, *k* and *q*, the worst; in fact, the latter sounds are frequently lost. The ear also requires a certain education; and the power of hearing varies surprisingly with the different ears and with different people. Singing always comes through with remarkable distinctness; and the sounds of a wind-instrument—the cornet or the bugle—are reproduced with startling force. A bugle sounded in London was heard distinctly over the large Corn Exchange of Basingstoke by a thousand people. This arises from the regularity as well as increased amplitude of the sonorous vibrations, and consequently from the regularity, uniformity, and increased strength of the currents of electricity.

IV. *Improvements.*

Every one who has the means at his disposal has been endeavouring to increase the power of this instrument. I should be sorry to enumerate the number of experiments I have tried, but all with vexatious, disappointing, and dispiriting failure.

One of the earliest efforts was made by Mr. Willmot, who hoped by increasing the number of diaphragms, coils, and magnets acted upon simultaneously, and joining up all those coils in series, to obtain a resultant effect that would magnify the out-going currents; but the result showed that, while the apparatus acted all right, the effect of displacement of each diaphragm decreased with their number, and the ultimate effect was the same as with one diaphragm. Mr. Willmot's instrument, which was made early in October last, is on the table; M. Trouvé, in Paris, seems to have been working on the same idea.

Increasing or varying the size, form, and strength of the magnet has produced little or no apparent improvement; for the resultant effect in all cases remained apparently the same.

The greatest effect is produced with a compound horseshoe magnet, which is indeed one of the earliest forms brought out by Mr. Bell. Here we have two coils, utilizing the maximum number of lines of force; and the effects produced are certainly the finest I have yet experienced. At Southampton, on the 14th inst., in a small office, Mr. Willmot's voice (he was in London) was heard distinctly by the seven or eight persons who were in the room at the time. Though I have made one with the largest and most powerful magnet I could obtain, the result has been as disappointing as in the previous cases. The telephone has certainly been brought to this country by Mr. Bell in almost its perfect theoretical form; he is still labouring to improve it; and I am sure we all wish him success.

V. *Applications.*

However small and however sudden the currents may be, the telephone records them with great accuracy; no known form of galvanometer or galvanoscope will do so.

It is admirably adapted for showing the currents of induction set up in contiguous coils or contiguous spirals. If reversals or intermittent currents be sent through one spiral while the other be gradually removed away, the rapidly diminishing effect of increased distance is very evident; indeed all the phenomena of magneto-electric induction are strikingly shown by its means. It is also admirably adapted as a detector in the bridge of a Wheatstone's balance to test short lengths of wire, and it will probably enable us to obtain a closer approximation to equality than we have yet secured; it also enables us to adjust condensers with great accuracy.

M. Niaudet, of Paris, has shown how it can be utilized to detect the presence of extremely feeble currents from doubtful sources of electricity. If currents from the supposed source be rapidly sent through one wire of a double-wound coil, and a telephone be fixed on the other running parallel to it, then the telephone would give evidence of their presence, which would be indiscernible on any other instrument.

It is admirably adapted also for testing leaky insulators and supports.

VI. *Inferences and Results.*

The telephone explodes the notion that iron takes time to magnetize and time to demagnetize. If time were occupied in magnetizing, notes would be changed or lost; but they are not altered. The notion of time is due to the action of induction in coils producing *reaction* and *extra currents.* This is proved by the insertion of an electro-magnet or of coils of wire in a telephonic circuit. While it is possible to speak through a cable 100 miles long laid out straight in the sea, it is impossible to speak through 20 miles when coiled in a tank.

Its delicacy has detected the presence of currents in wires contiguous to wires conveying currents, which have always been suspected, but have been evident only on wires running side by side for several miles (say two hundred) on poles or in well insulated cables. In fact, the most delicate apparatus has hitherto failed to detect the presence of these currents by induction in short underground wires; but the telephone responds to these currents when the wires run parallel for only a few feet. Thus, between one floor and another floor, at the General Post Office, it has been impossible to converse by means of the telephone through a wire, owing to the presence of these currents of induction from the innumerable working wires contiguous to it, and through some of the underground pipes of the streets of London sounds are inaudible when the wires are working. In fact, two small-sized gutta-percha wires, *one foot long,* were lashed side by side by Mr. Marson; and when battery currents were sent through one, induction currents were distinctly heard on a telephone fixed on the other. Indeed this induction between wire and wire, has proved the most serious obstacle to the practical introduction of the instrument. But it is not altogether irremediable on underground wires; it can be surmounted in three ways:—

1. By increasing the intensity of the transmitted currents so as to overpower the currents of induction, and by reducing the sensitiveness of the receiving apparatus so as to make the instrument insensible to currents of induction though responsive to telephonic currents.

2. By screening the wire from the influence of induction.

3. By neutralizing the effects of induction.

1. Mr. Edison in America has partially succeeded in effecting the first cure ; but his results, though promising, have not yet reached a practical point.

2. I have overcome the second difficulty in a way that will now be described.

Let 1, fig. 3, be a wire used for telephonic purposes, and 2

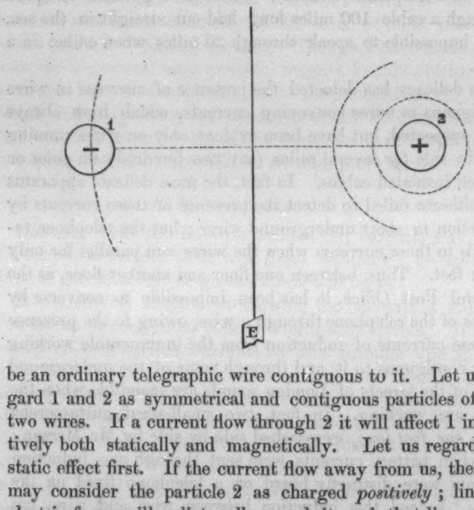


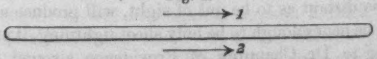
Fig. 3

be an ordinary telegraphic wire contiguous to it. Let us regard 1 and 2 as symmetrical and contiguous particles of the two wires. If a current flow through 2 it will affect 1 inductively both statically and magnetically. Let us regard the static effect first. If the current flow away from us, then we may consider the particle 2 as charged *positively* ; lines of electric force will radiate all around it, and that line which passes through 1 will inductively charge that particle *negatively*. This influence being felt all along the wire, a current in the reverse direction to that in 2 will flow through 1. The reverse would occur if we assumed the primary current to flow in the other direction. Hence, an induced current will flow through 1, whenever the current in 2 commences and whenever it ceases. Now, if we place between 1 and 2 a screen of metal, or other conducting matter, in connexion with the earth, then the line of electric force, instead of passing through 1, will terminate at the screen. Hence, if we surround the wire 2 with a covering or sheath of metal, or if we submerge it in water, all effects of static induction will cease between 1 and 2. In water they are not entirely eliminated, for water is a very poor conductor; but they are so reduced by its influence, as my experiments between Manchester and Liverpool and between Dublin and Holyhead have shown, that, if the water or wet serving had been a perfect conductor, they would have been removed as far as regards static induction.

But we have to regard magnetic induction as well. Besides establishing a field of electric force around 2, a current flowing through that wire establishes a magnetic field around it, whose lines of force are circles, and whose directions are at right angles to the lines of electric force. Let us regard that line of force cutting 1. Each time a current commences, and each time it ceases, in wire 2, a line of magnetic force cuts wire 1, and produces in that wire a current of induction in the same direction as that produced by static induction. Now, if we make the screen of iron, those lines of force terminate in the iron and wire 1 is freed. Hence, if we sheath the wire 1 with iron, it is not only freed from the effects of static induction by being surrounded by a conductor in contact with the earth, but it is shielded from the effects of magnetic induction by its sheath of iron. Hence both effects of induction are entirely removed.

3. They can be neutralized by means of a return wire, using this return wire instead of the earth. If 1 and 2, fig. 4, be

Fig. 4.



two wires running side by side, then the current set up by induction from neighbouring wires in one wire is neutralized by the currents set up in the other side.

But this assumes either that the disturbing wires are at an infinite distance from 1 and 2, or that 1 and 2 are infinitely near each other. All attempts to use return wires on existing poles, in cables, or in underground wires have utterly failed to do away with inductive disturbance; but Mr. Bell has had a single gutta-percha wire carrying two conductors made which very nearly fulfils the conditions and gives excellent results.

The extreme delicacy of the instrument has introduced a disturbance from another cause, viz. leakage. Wires on poles are supported by glass, porcelain, and earthenware insulators; but the best support that was ever devised is but a poor insulator in wet weather. Currents escape over their surface from ~~the wire~~ they support; and these leakage currents find their way into telephonic circuits. Hence a telephone circuit which may work ~~well in~~ dry fine weather will prove absolutely unworkable in wet weather.

Another source of trouble arises from what are technically called "bad earths." It is almost impossible to make a perfect connexion with the earth. There is always some resistance at that point; so that if two wires terminate on the same earth-plate, the one being a working circuit and the other a telephone-circuit, some currents from the former are sure to pass through the latter and disturb the telephone. A return wire perfectly cures this evil.

There are other disturbing elements that are peculiar. Earth-currents, which are always present in the wires, produce a peculiar crackling noise, similar to that produced by a current from a single fluid battery such as a Smee or a Leclanché, not unlike the rushing of broken water. This is due to the polarization of the earth-plate, as the sounds produced by a battery-current are due to the polarization of the negative plate. When auroras are present these earth-currents become very powerful, and the sounds are much intensified. The effects of thunderstorms are very peculiar: a flash of lightning, even though so distant as to be out of sight, will produce a sound; and if it be near enough to be only sheet lightning, it produces, according to Dr. Channing, of Providence, a sound like the quenching of a drop of melted metal in water, or the sound of a distant rocket. Moreover he says that this sound is heard before the flash is seen, proving the existence of some inductive effect in the air prior to the actual discharge. The telephone thus becomes an admirable warning of the approach of a thunderstorm.

Sometimes a peculiar wailing sound is heard, which an imaginative correspondent of mine likened to "the hungry cry of newly-hatched birds in a nest." I am inclined to think that it is due to the swinging of the wires across the magnetic lines of force of the earth. It is not difficult to conceive that these vibrations may succeed each other in the necessary rhythmic order to produce musical tones.

The wires are never free from sound; and every change of temperature or of the electric condition of the atmosphere is recorded on this delicate apparatus.

The expansion of the iron diaphragm under the influence of the warm and damp breath when the telephone is first raised to the lips preparatory to talk is very marked; it produces a faint rustling shiver.

Immediately on the introduction of the instrument, great anxiety was felt to learn its performance on submarine cables. A telephone was sent to Guernsey, and Mr. Willmot went to Dartmouth, those two places being connected by a cable 60 miles long. Conversation was carried on, the articulation being perfect though slightly muffled. This was a surprise; for it was felt that the static induction of a cable, by its retarding influence, would have prevented articulation by lengthening the waves of electricity and rolling them up as it were. Through the kindness of Messrs. Latimer Clark, Muirhead, and Co. I was able to repeat these experiments on an artificial Atlantic cable, constructed to duplex the direct United-States cable. With Mr. Willmot at one end and myself at the other, there was no difficulty in speaking up to 100 miles, though the muffling effect of induction was evident. Beyond this distance up to 150 miles muffling commenced to seriously impede conversation, and the sounds diminished considerably in strength: it was like talking through a thick respirator. The effect diminished rapidly up to 200 miles, beyond which articulation became impossible, though singing was distinctly heard; indeed singing was heard through the whole length of the cable, 3000 miles long; but this was traced to a secondary cause, it being due to the induction of condenser on condenser. Nevertheless there is no doubt that singing can be heard through a much greater length than speaking, due to the greater regularity of the successive waves of electricity.

I subsequently experimented on the underground wires between Manchester and Liverpool, a distance of about 30 miles;

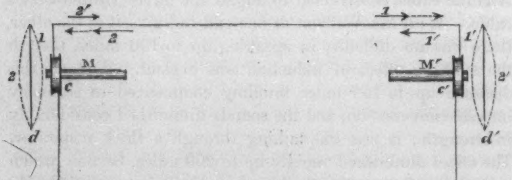
and through this length we had no difficulty whatever in speaking. Again, between Dublin and Holyhead, through the cable 67 miles long, we spoke with ease, singing coming through with remarkable power and effect. This cable contains 7 distinct conductors. When one wire was used for the telephone, the sounds could be heard on every other wire, but in a feebler degree. When the other wires were working with the ordinary telegraphic apparatus, induction was evident, but not sufficiently intense to stop conversation. Each wire would be surrounded with a wet serving of hemp; but this was not of sufficient conducting-power to entirely screen the effect of induction. The same effect was experienced between Manchester and Liverpool, where the wires are made up into cables of 7 conductors served outside with tarred hemp.

The conclusion that I have come to is, that conversation might be held through a single wire cable 200 miles long with the apparatus that we now have; what new apparatus will do no man is rash enough to predict.

The reason for this surprising result is not difficult to explain:—

Let the disk *d*, fig. 5, be impressed forwards by a sonorous vibration, it will generate in the coil *c* a positive current,

Fig. 5.



which, flowing through the line, will pass through the coil *c′* and attract the disk *d′*. Now the effect of induction is to retard or prolong the effect of the positive current 1; but the motion of the disk *d′* has itself produced a current in the reverse direction to the first current; and this neutralizes the prolongation due to induction, and so helps to clear the line for the next signal, which passes through precisely the same process; and hence the vibrations of the second disk tend to produce currents which diminish materially the effects of induction, and so render possible conversation to distances that far exceed anticipation.

The extreme delicacy of Bell's apparatus has been shown in various ways; for instance:—

Extract from a letter from T. A. Edison, *dated November* 25, 1877.

"I made a pair of telephones that work with copper diaphragms: it is on the revolving-copper-disk principle of Arago.

"I find that a copper diaphragm may replace the iron in Bell's. Copper must be $\frac{1}{32}$ in. thick. It is very low with copper in both; but if the receiver is one of the regular kind, and the transmitter is a copper diaphragm, you can carry on conversation with ease both ways; but with the pair I have made the talking is loud, as I have several dodges on it."

I repeated these experiments; but the effect was so feeble as to be scarcely distinguishable, and, although interesting from a scientific point of view, it was of no practical value.

Mr. James Blyth has independently repeated the experiment, and has shown that wood, paper, and india-rubber produce similar effects. These effects are probably due to the fact that diamagnetic bodies have a similar though feebler influence, in varying the direction of lines of magnetic force, to magnetic bodies.

Again, I have spoken distinctly and easily with telephones without any permanent magnet whatever, the core of the coil being of soft iron; but this effect was probably due to the impurity of the iron, residual magnetism remaining in it. Dr. Blake, of Boston, has spoken easily when the core was a piece of soft iron placed in the direction of the dip.

XXV. *The Production of Thermoelectric Currents in Wires subjected to Mechanical Strain.* *By* G. W. VON TUNZELMANN, *Holder of the Clothworkers' Exhibition in Chemistry and Physics at University College, London.*

THE following inquiry was suggested by some observations recorded in a paper of Sir William Thomson's on the Electrodynamic Qualities of Metals, in the 'Philosophical Transactions' for 1856; and the object in view was to investigate the conditions under which thermoelectric currents are produced in a circuit composed of a single metal when one portion of the metallic conductor is subjected to a strain and the junctions of the strained and unstrained portions are maintained at different temperatures.

The experiments were made upon wires of iron, steel, and copper, the copper wire employed having been obtained from Messrs. Johnson, Matthey & Co. as chemically pure.

Two tin cans were obtained open at the top, and pierced at the bottom by necks into which india-rubber corks were inserted; and through slits in these the wires were passed. The wire was fastened by a clamp in the lower can, and was grasped in the upper one by a pair of wire-drawing dogs attached to the shorter arm of a lever, to the longer arm of which was attached the weight by which the strain was produced. In the earlier experiments ordinary weights were used; but ultimately these were rejected, as it was found impossible to apply and remove them in a sufficiently gradual manner to prevent a certain amount of shock, which introduced complications.

In the arrangement finally adopted, there was attached to the longer arm of the lever a tin can open at the top, and having at the bottom a neck fitted with an india-rubber tube, which could be closed by merely bending it up and hitching it in a hook attached to the can for that purpose. The strain on the wire was then produced as gradually as was desired, by pouring in measured quantities of shot; and it could be removed as gradually by letting the shot run out by the india-rubber tube.

The two cans through which the wire passed were filled with water, the water in the upper can being kept at the temperature of 100° C. by means of a gas-burner, while that in the lower can could be kept for a considerable time at a uniform temperature by allowing a current of water, of the same temperature as the place of experiment, to circulate through it.

The extremities of the experimental wire were bent round in a large curve and brought close together; they were then tied to the extremities of two covered copper wires connected, through a four-way key, with a Thomson's galvanometer having a resistance of between one and two ohms. The junctions were then placed side by side separated by thin paper, and wrapped up in cotton-wool, as was done by Thomson in his experiments, to prevent the production of currents by the unequal heating of the two junctions.

Before being used the wires were annealed:—the iron and steel wires by being heated to redness in an iron tube, through which a current of coal-gas was passing to prevent oxidation; the copper wire by being slowly passed through a Bunsen flame, as it was found that the exposure of the copper at a red heat to the current of coal-gas produced an effect similar to that known as over-poling in the process of refining copper, the wire being rendered so brittle as to break with the least strain.

Thomson found in his experiments that when a weight was applied so as to produce a state of strain in a portion of the wire, and the two junctions of strained and unstrained portions were kept at different temperatures, in iron and steel wire a current was produced the direction of which was from the unstrained to the strained portion across the hot junction, while in copper wire the current was in the opposite direction. When the weight was removed the result was in either case a weaker current in the reverse direction.

Some experiments of the same nature have also been made by M. le Roux, and described in the *Annales de Chimie et de Physique*, 4th series, vol. x. p. 201 (1867). He obtained results of the same nature as Thomson—with the notable difference that in iron and steel wires he got a current from strained to unstrained across the hot junction, while in copper wire the current was from unstrained to strained across the hot junction. On comparing the descriptions of the experiments, it appeared that Thomson had always made his experiments with comparatively small strains, while Le Roux had strained his wires very nearly to the breaking limit. This at once suggested a possible explanation of the apparent discrepancy between their results; and on making the experiments, it was found that as the strain was gradually increased the current was increased, as in Thomson's experiments, but only up to a certain limit. When the strain was increased beyond this limit there was a gradual decrease in the current; and if the strain was very carefully increased, the direction of the current was reversed shortly before the breaking strain was reached.

During the experiments, it was very soon observed that after a weight had been added the current did not remain constant, but gradually diminished; while at the same time there were variations of small period in the strength of the current, which were greater when the weight was added suddenly, and scarcely perceptible when it was very carefully and slowly added by pouring in shot; these variations gradually ceased when the apparatus was not disturbed. A very gentle and gradual addition of weight diminished these variations, which always died away more rapidly when there was a heavy strain on the wire. Clutching the wire in the "dogs" also set up these variations, which were allowed to subside before beginning the experiment. These results suggested that the production of the current might be due to a process of change in the molecular state of the wire; it was found, however, on examination that there was a permanent effect which could not, as far as I can see, be produced in that way, whatever may have caused the temporary effect.

Where the results obtained at different times had not to be compared, the current is generally given in terms of the deflections of the galvanometer; but where such comparison was necessary, the value of the deflections was determined at each experiment in terms of a standard current obtained by sending a current from a Daniell's cell through a definite resistance.

For the sake of brevity, U.S. will be written for "from unstrained to strained across the hot junction;" and the opposite direction of the current will be denoted by S.U. The following letters are used in the description of the experiments:—

W = tension applied to wire in pounds, = 3 times weight actually applied to lever;
M = number of measures of shot effective in stretching wire, = 3 times number actually applied to lever;
Θ = temperature of lower can;
D = mean deflection of galvanometer;
C = strength of current in terms of the standard current.

A considerable number of preliminary experiments were made to verify Thomson's results and to determine the best form of apparatus, the arrangement ultimately adopted being that already described. These experiments (which are not described here) gave a general idea of the phenomena to be looked for. The alteration of resistance from strain is not taken into consideration, as H. Tomlinson's experiments, Proc. Roy. Soc. 1876 (vol. xxv. p. 451), have shown that it is too small to have an appreciable influence upon the results.

Experiment 1.—An iron wire ·46 millim. diameter. Θ = 16°; W = 31·5. The result is given in the accompanying Table, the direction of the current being U.S., the first reading being taken immediately after the weight was applied. It will be observed that the current does not reach its full strength immediately upon the application of the weight, but rises rapidly to a maximum, and then gradually falls to a strength at which it remains steady.

Time (minutes).	D.
0	2·5
5	6
10	3
15	2
20	2
25	2

Experiment 2.—A similar wire. Θ = 16°. The readings were taken immediately after the application of the weight. The sign * means that there is a deflection, but too small to be measured.

W.	D.	Direction.
6	*	U.S.
9	5	U.S.
12	3·5	U.S.
15	3	U.S.
18	*	S.U.
21	wire broke.	

It will be observed that the direction of the current changes just before the wire breaks.

Some steel wire was now taken; and as it was found almost impossible by the most careful annealing to get a piece of wire arranged in the apparatus which should give no deflection before the application of the weight, the initial deflection was noted in each case.

Experiment 3.—A steel wire ·81 millim. diameter. $\Theta = 16^\circ$. Initial deflection = 20 S.U. W = 31·5. After the application of the weight the deflection reversed its direction to U.S. The result is given in the following Table.

Time (minutes).	D.
2	10
3	12
4	13
5	15
6	18
24	10
25	9
50	9
90	5
130	3

The apparatus was then left for about 90 hours with the weight attached; Θ being still 16°, there was now a deflection of 15 S.U. The weight was then removed, and the deflection fell rapidly and changed to U.S. The subsequent deflections were as follows:—

Time from removal of strain (minutes).	D. U.S.
1	2
2	3
3	4
4	6
5	7
6	8
14	8
20	10
25	7
30	3

In both cases we observe that the current gradually rises to a maximum and then falls.

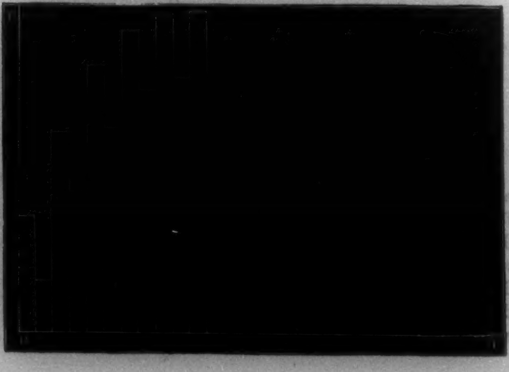
Experiment 4.—A steel wire ·98 millim. diameter. $\Theta=15°$. Initial deflection = 10 S.U. On the addition of a weight of 42 lbs., the deflection changed rapidly to 14 U.S., and in about an hour fell to 8 U.S., and in 40 hours to 3 U.S.

Experiment 5.—A steel wire ·6 millim. diameter. $\Theta=13°$. Initial deflection = about 1 U.S. W = 63 lbs. Direction of current after application of weight U.S. The weight was now left suspended for about 40 hours; but the apparatus received an accidental jar before the permanent deflection could be ascertained. The weight was then removed, causing a deflection of 8 S.U., gradually increasing to 11, and then decreasing much more slowly than it had increased.

Time from removal of strain (minutes).	D.
3	3·5
6	4·5
9	3·5
12	2·5
15	1·5
18	·87
36	*

The effect of rapidly putting on and taking off the weight a number of times in succession was then tried; and it was found that each time the weight was put on the deflection diminished, while each time that it was taken off the deflection was increased up to a certain limit. The immediate increase produced by taking off the weight was greater than the immediate decrease produced by putting it on; so that on the whole there was a large increase in the current, the deflection being got up in this way to nearly 30 S.U., falling again very rapidly if the weight were left attached to the wire. Under these circumstances the deflection went down rapidly to zero, changed sign, rose to a maximum, and then again began to diminish, passed through zero in the opposite direction, and so continued to perform excursions in alternate directions, and very rapidly decreasing in extent. When the weight was permanently removed the deflection of the galvanometer died out much more slowly, and the changes of sign were only just perceptible. These phenomena confirm the conclusion to which I was led by the former experiments, that there is, besides the main effect, a transient effect produced by altering the strain on the wire; and this transient effect appears to me to be due to the molecular state of the wire making a partial return after the first shock towards its primary condition, just as the immediate deflection of a spring suddenly stretched by a weight is greater than when it has come to rest in its position of equilibrium. The changes of sign in the current as it gradually comes to its final state after the wire has been violently disturbed, as in the last experiment, as also the fact of there being a permanent as well as a temporary effect, seem to render this hypothesis more probable than that the current is actually produced by a change in the molecular state of the wire.

The phenomena obtained in the last experiment will be rendered more clear by a diagram.



The intervals between taking off and putting on the weight were approximately equal. These are therefore represented by equal distances along the axis O T; and the strength of the current is set off along the axis O C. Starting from the point O, at the beginning of the experiment, with the weight attached to the wire as it had been left, then at any time the broken line

- - - - - represents the permanent change in the current produced by taking off or putting on the weight;
...... represents the temporary change;
—— represents the resultant strength of the current, being the sum of these two components.

The curve A represents the change in the current when the weight is left permanently attached; and the curve A′ represents the change in the current when the weight is permanently removed.

At this stage in the experiments the method of measuring the current-strength in terms of a standard current was adopted. The battery used as a standard was a "sawdust" Daniell's (Menotti's) cell; and the strength of the current was approximately that produced by 1 volt through 10,000,000 ohms, or 10^{-8} C.G.S. unit. The measurements of the Tables are given in millionths of a C.G.S. unit.

Experiment 6.—A similar steel wire. $\Theta = 16°$. Initial deflection barely perceptible S.U. Weight of 30 lbs. left on about 40 hours.

It was observed that at the time of making the experiment the weight was making small oscillations; and this appeared to be the cause of the deflections making small oscillations about a mean value. At the end of an hour and a half the oscillations of the weight and also of the deflection had ceased, the latter remaining steady at 5, indicating a current ·007 U.S. The weight was now made to perform vibrations of small amplitude, upon which the oscillations of the deflection were greatly increased both in number and amplitude, and the mean deflection was at the same time somewhat increased. If the vibration of the weight be suddenly stopped, it is some little time before a decrease is perceived in the oscillations of the deflection.

After setting the weight in gentle vibration, the effect in causing oscillations in the deflection was observable in less than a minute. If the vibrations of the weight are kept up for some time, the mean deflection is increased up to a certain limit, as before described. If the vibrations of the weight are increased in amplitude, the oscillations of the deflection become much more irregular, and the limits of variation become greater.

Experiment 7.—A similar wire. $\Theta=12$. Initial current ·0014 U.S. A weight of 3 lbs. was now attached; and at the end of two minutes there was a current ·0052 S.U., falling at the end of an hour and a half to ·0034 U.S. The weight was then increased by 3 lbs. at a time and the deflections taken immediately, with the results given in the accompanying Table:—

W.	C.	Direction.
6	·0038	U.S.
9	·0019	U.S.
12	·0014	U.S.
15	·0012	U.S.
18	·0012	U.S.
21	·0012	U.S.
24	·0012	U.S.
27	·0010	U.S.
30	·0002	U.S.
33	*	S.U.

In the experiments after this the weights are given in terms of measures of shot, each of which weighed about 7480 grains.

Experiment 8.—A similar wire. 33 measures left on for about 40 hours. $\Theta=12°$. Deflections read immediately after removal of weight. Direction of current S.U. There was no initial deflection.

M.	C.
33	·0095
30	·0046
27	·0035
28	·0039
21	·0049
18	·0060
15	·0067
12	·0074
9	·0084
6	·0091
3	·0098
0	·0105

Experiment 9.—A similar wire. $\Theta=12°$. No initial deflection. Deflections read immediately after application of weight.

M.	C.	Direction.
3	·0025	U.S.
6	·0025	U.S.
9	·0021	U.S.
12	·0014	U.S.
15	·0014	U.S.
18	·0014	U.S.
21	·0014	U.S.
24	·0014	U.S.
27	·0011	U.S.
30	·0007	U.S.
33	·0004	S.U.
36	·0014	S.U.

Experiment 10.—A steel wire ·47 millim. diameter. $\Theta=12°$. Initial deflection 4 U.S. On attaching the empty can for containing the shot to the end of the lever the deflection increased to 20 U.S., falling to 14·5. The strain was gradually increased by pouring shot into the can until the wire broke. The deflection changed very little until the wire began to stretch, when the deflection fell very rapidly, passed through zero, and went up to about 40 S.U.

The more rapid the stretching the stronger is the current produced. When the strain was slightly lessened, so as to stop the stretching, the deflection fell very quickly to 20 S.U. On removing the strain the deflection fell rapidly, passed through zero, and went up to 2 or 3 U.S., making irregular vibrations. The weight was replaced and additional shot poured in very slowly. The deflection almost instantaneously changed to about 2 S.U., which increased slightly until the wire broke.

Experiment 11.—A copper wire ·24 millim. diameter. $\Theta=15°$. Initial deflection 1 S.U.

M.	D.
0	1
3	1
6	3
9	3
12	3
15	4
18	4
21	2·5
24	2·5
27	2
30	1·5
33	1·5
36	1·5
39	1·5
42	1·5

The direction of the current was S.U. Several small weight were added to the can; but the deflection remained steady at 1·5. In copper wire, no fall in the deflection was observed when the weight was left suspended for some time.

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XXVI. *On the Influence of Temperature on the Passage of Air through Capillary Tubes.* *By* FRANCIS GUTHRIE, *LL.B.*[*]

IN using "Marsh's" apparatus for testing for arsenic, it may be noticed that, when heat is applied to the exit-tube to decompose the arsenuretted hydrogen, the liquid rises in the tube which supplies the sulphuric acid, thus leading to the supposition that the passage of the gas through the exit-tube is checked by the increase of temperature, thereby producing increased pressure. This observation suggested the following experiments on the effect of heat on the passage of gases through capillary tubes.

The apparatus used was as follows:—From a vessel, A, water drops into a funnel, *b*, causing a continued overflow.

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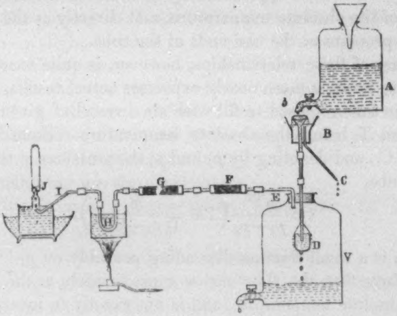
[*] Communicated to the Physical Society, April 13, 1878. A note of the results was communicated to the British Association, 1876.

The overflow falls into the concentric funnel B, and escapes by the tube C. The middle of the funnel-tube is removable, and may be replaced by tubes of any required lengths. The lower end of the funnel-tube passes air-tight through the cork of a bottle, V, and has hanging from its end a little thimble of glass, D. By this means, whatever amount of water has entered V, the pressure in V is that due to the difference of height of the water in *b* and D. The air from V is dried by two chloride-of-calcium tubes, F and G, and then passes through the experimental capillary tube H, which can be heated. Thence it passes down the tube I and is collected over water in the tube J, which has a marked stricture. The vessel in which J stands is always overflowing.

Fig. 1.



It was found that the utmost attention was required to keep the air perfectly dry. A joint of caoutchouc in water is found to be porous to water near its boiling-point, the water probably penetrating as a vapour. As the slightest intrusion of water would vitiate the experiment, paraffin was used in such cases.

The first point to be decided on was, whether heating a current affected its rate of motion independently of its friction. At first sight this seemed not to be impossible; the expansion of the air while its temperature is being raised might, it was thought, react on the air behind it and thus check its outflow. Experiments, however, showed that this was not the case, and that the effect of heat in checking the current is due solely to its influence on gaseous friction.

It was found that the amount of air passing down a given capillary tube varies approximately in the inverse ratio of the square of the absolute temperature, and directly as the difference of pressure at the two ends of the tube.

Neither of these relationships, however, is quite exact; the following formula more nearly expresses actual results. Calling t the time required to fill with air a vessel of given capacity, and T being the absolute temperature reckoned from $-273°$ C., and denoting by p_1 and p_2 the pressures at the ends of the tube,

$$t = \frac{\alpha T^2}{p_1 - p_2}\left(1 + \frac{\beta}{T(p_1 - p_2)^n}\right),$$

where α is a small fraction depending probably on p_1.

The facts that the time varies approximately as the square of the absolute temperature, and is not exactly in inverse proportion to the difference of pressure, are worthy of notice; and their theoretical investigation will throw some light on the molecular theory of gases. The fact that the temperature affects the time according to the square of the absolute temperature is consistent with known molecular laws. It has been shown that the viscosity of air and its consequent shearing friction is in proportion to T. And it is obvious from the fact that the volume of a given mass of air is directly as its absolute temperature, that the time required for the passage of a given quantity of air through a given tube at a given pressure should vary as T^2.

More anomalous are the results that the velocity does not exactly follow the simple law that the rates of passage at a given temperature are in proportion to the difference of pressures at the ends, but that the time of passage of a given mass of air is shortened by increased pressure in a somewhat greater proportion than the increase of pressure. The deviation from the law of inverse proportion is only slight, and obviously belongs to a term having a small absolute factor. But an inspection of the results will show that its existence is unmistakable.

To examine the effect of simply raising the temperature, the following experiments were made:—

(1) The current was heated in a wide tube before reaching the capillary tube, being afterwards cooled again to the temperature of the outer air. *Result*:—the time of passage of a given mass of air was slightly increased.

(2) The current was heated after passing the capillary tube. *Result*:– a slight decrease in the time of passage of a given volume. The decrease was only such as might be accounted for from the fact that the air was not completely cooled again.

(3) The heating and cooling of the current in the capillary tube. *Result*:—an increase of time apparently proportional to the length of the tube heated.

The following are the experiments:—

(1) Whole current at atmospheric temperature 22° C.

(*a*) $t=659''$
(*b*) $t=656''$ Mean $657''\cdot5$.

The current was then heated to 100° C. in a wide tube before entering the same capillary tube.

(*a*) $t=670''$
(*b*) $t=668''$ Mean $669''$.

The slight increase of time here indicated was probably due to the fact that the air current had not altogether regained its normal temperature before reaching the capillary tube.

(2) Whole current at atmospheric temperature 21° C.

(*a*) $t=157''$
(*b*) $t=156''$ Mean $156''\cdot5$.

The current was then heated to 100° C. in a wide tube after passing through the capillary.

(*a*) $t=153''$
$t=155''$ Mean $154''\cdot0$.

(3) Capillary tube partly immersed in a paraffin-bath at 200° C. The end cooled to 22° C.

$t=10055''$.

More of the tube being heated,

(*a*) $t=1098''$
(*b*) $t=1094''$ Mean $1096''$.

The effect of heating and cooling of the same current in different tubes in the same circuit was then examined. The same tubes were timed separately and in conjunction at the same and at different temperatures.

Tube.	Temperature.	Time.
1	24·5° C.	60″
2	”	57
3	”	58
1	100	89
2	”	81
3	”	82
1+2	24·5	117
”	100	173
1 +2+3	100 21	203
1+2 3	100 21	228

These results show that the resistance of the sum is very nearly the sum of the resistances, whether all the tubes are at the same temperature or some at one temperature and some at another.

In order to ascertain whether the rate of passage followed any special law at the beginning or end of the tube, the time of the passage of a given mass of air thrust through a given tube at a given pressure and temperature was ascertained; the tube was then divided into parts, and the time of the passage of the same bulk of air through each part was measured.

	20° C.	100° C.
Entire tube	372″·5	563″
Part 1	89·5	133·3
” 2	117·5	180·0
” 3	63	96·5
” 4	101	152
” 1+2	208·5	315·6
” 3+4	165	246·6

From this Table it is seen that, within the limits of experimental error, the time taken for the passage of a given bulk of air through the entire tube is equal to the sum of the times taken for the passage of the same amount of air through each of its parts.

A similar experiment with a tube divided into a greater number of parts was then made. The original tube was about 600 millims. long.

(*a*) $t=85''$
(*b*) $t=83''$ Mean $84''$.

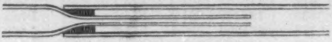
The tube was then divided without loss into 21 parts; these were connected by caoutchouc and covered with paraffin.

(*a*) $t=86''$
(*b*) $t=85''$ Mean $85''\cdot5$.

These experiments show that the terminations of the tubes exert no special influence on the passage of the current.

A conical or trumpet-shaped tube was then examined, the arrangement being according to fig. 2. The following were the results.

Fig. 2.



Wide end towards greatest pressure.

(*a*) $t=183''$
(*b*) $t=184''$ Mean $183''\cdot5$.

Narrow end towards greatest pressure.

$t=184''$.

This shows that the rate is the same both ways.

The foregoing experiments having shown that the effect of temperature on the rate of a current was to be looked for in its influence on fluid-friction, the next thing was to determine the relation between temperature and time, other things being the same. For this purpose a capillary tube, through which a current was passing at a constant pressure, was subjected down its entire length to various temperatures—care being taken that the air should arrive at the entrance of the capillary tube at the temperature of the tube itself, so that the current might be of the same temperature throughout the entire length of the capillary tube. The times of passing of a given quantity of air for different temperatures were noted; and some of the results are subjoined.

Temp. Centigrade. C.	Absolute temp. T.	T^2.	Time. t.	$\frac{T^2}{t}$.	$\Delta\left(\frac{T^2}{t}\right)$.	$\frac{T}{t}$.	$\frac{T(T+94)}{t}$
I. Pressure 315 millims. of Water.							
−20	253	64009	119″	538	12	2·42	712
0	273	74529	135·5	550	2	2·27	713
21	294	86436	156·5	552	15	2·13	705
60	333	110889	195·5	567	11	1·88	703
100	373	139129	240·5	578	36	1·65	696
200	473	223729	364·5	614	5	1·37	712
240	513	263169	425	619		1·29	713
II. Pressure 1000 millims. of Water.							
20	293	85849	110	784·5	12·0	2·663	1035
40	313	97969	123	796·5	10·0	2·545	1036
60	333	110889	137·5	806·5	7·9	2·422	1034
80	353	124609	153	814·4	8·8	2·307	1031
100	373	139129	169	823·2	11·6	2·207	1031
120	393	154449	185	834·8	7·9	2·124	1035
140	413	170569	202·4	842·7	3·8	2·040	1034
160	433	187489	221·5	846·5	9·4	1·955	1030
180	453	205209	239·75	855·9	9·6	1·889	1034
200	473	223729	258·5	865·5		1·833	1035
							1033·5

These Tables show—

(1) That the time varies approximately as the square of the absolute temperature. This appears from the approximate equality of the numbers in column 5.

(2) That the variation of the time deviates from the law of squares by a term approximately proportional to the temperature. This is shown by the average equality of the differences in column 6.

(3) That the formula connecting the time and the temperature is very nearly

$$t=d\mathrm{T}(\mathrm{T}+\beta),$$

where β seems to depend on the pressure p_1-p_2.

From the above series of experiments, however, the exact connexion between β and p_1-p_2 is not obvious; possibly it may be of the form

$$t=\alpha\mathrm{T}\left(\mathrm{T}+\frac{\beta}{(p_1+p_2)^3}\right).$$

The next series of experiments had in view the more exact determination of the relation between p_1-p_2 and t.

To obtain these results, it was necessary to determine the effect of capillarity and bubble-tension on the exit of the air through the final orifice.

It was found from experiment that these forces were very nearly equivalent to a pressure of 22 millims. The depth of the exit-orifice under the surface of the water over which the air was collected had, of course, to be allowed for.

The experiments gave the following results:—

Temperature 20° C.

	p_1-p_2.	t.	$(p_1-p_2)\times t$.	$\Delta(p_1-p_2)t$.
	millim.			
I.	+15	3945″	59175	
	76	719	54644	−4531
	157	344·5	54086	− 558
	303	180·5	54691	+ 605
	513	105	53865	− 826
	656	81	53136	− 729
	852	61·75	52611	− 518
	1205	43·6	52538	− 73
II.	200	426·5	85300	
	400	209·5	83800	−1500
	600	139 .	83400	− 400
	800	103·6	82933	− 467
	1000	82	82000	− 933
III.	200	563·6	112733	
	400	278 .	111200	−1533
	600	184·6	110800	− 400
	800	137·3̇	109866	− 934
	1000	108	108000	−1866
	1200	89	106800	−1200

The approach to equality in the amounts in column 3 shows that the time varies nearly in the inverse ratio of the difference of pressures. The gradual diminution of the number in that column visible, on the whole, shows that this law is slightly deviated from, and that the time diminishes somewhat more rapidly than the reciprocal of the pressure—a conclusion which is at variance with the results arrived at by Bunsen for the passage of gases through porous plugs.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

JULY 1878.

XXVII. *On the Physical Action of the Microphone.*

By Professor HUGHES.*

IN the paper read on the 9th of May before the Royal Society, I gave a general outline of the discoveries I had made, the materials used, and the forms of microphone employed in demonstrating important points. I have made a great number of microphones, each for some special purpose, varying in form, mechanical arrangement, and materials. It would require too much time to describe even a few of them; and as I am anxious in this paper to confine myself to general considerations, I will take it for granted that some of the forms of instrument and the results produced are already known.

The problem which the microphone solves is this—To introduce into an electrical circuit an electrical resistance, which resistance shall vary in exact accord with sonorous vibrations so as to produce an undulatory current of electricity from a constant source, whose wave-length, height, and form shall be an exact representation of the sonorous waves. In the microphone we have an electric conducting material susceptible of being influenced by sonorous vibrations; and thus we have the first step of the problem.

The second step is one of the highest importance: it is essential that the electrical current flowing be thrown into waves of determinate form by the sole action of the sonorous vibrations. I resolved this by the discovery that when an electric conducting matter in a divided state, either in the form of powder, filings, or surfaces, is put under a certain slight pressure, far less than that which would produce cohesion and more than would allow it to be separated by sonorous vibrations, the following state of things occurs. The molecules at these surfaces being in a comparatively free state, although electrically joined, do of themselves so arrange their form, their number in contact, or their pressure (by increased size or orbit of revolution) that the increase and decrease of electrical resistance of the circuit is altered in a very remarkable manner, so much so as to be almost fabulous.

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* Read June 8, 1878.

The problem being solved, it is only necessary to observe certain general considerations to produce an endless variety of microphones, each having a special range of resistance.

The tramp of a fly or the cry of an insect requires little range but great sensitiveness; and two surfaces, therefore, of chosen materials under a very slight pressure, such as the mere weight of a small superposed conductor, suffice; but it would be unsuitable for a man's voice, as the vibrations would be too powerful, and would, in fact, go so far beyond the legitimate range that interruptions of contact amounting to the well-known "make and break" would be produced.

A man's voice requires four surfaces of pine charcoal, as is described in my paper to the Royal Society, six of willow charcoal, eight of boxwood, and ten of gas-carbon. The effects, however, are far superior with the four of pine than with either the ten of gas-carbon or any other material as yet used. It should be noted that pine wood is the best resonant material we possess; and it preserves its structure and quality when converted into the peculiar charcoal I have discovered and described.

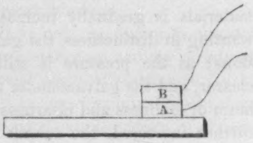
It is not only necessary to vary the number of surfaces and materials in accordance with the range and power of the vibrations, but these surfaces and materials must be put under more or less pressure in accordance with the force of the sonorous vibrations. Thus for a man's voice the surfaces must be under a far greater pressure than for the movements of insects. Still the range of useful effect is very great, as the boxes which I have specially arranged for man's voice are still sensitive to the tick of a watch.

In all cases it should be so arranged that a perfect undulatory current is obtained from the sonorous vibrations of a certain range. Thus, when speaking to a microphone transmitter of human speech, a galvanometer should be placed in the circuit, and, while speaking, the needle should not be deflected, as the waves of + and − electricity are equal, and are too rapid to disturb the needle, which can only indicate a general weakening or strengthening of the current. If the pressure on the materials is not sufficient, we shall have a constant succession of interruptions of contact, and the galvanometer-needle will indicate the fact. If the pressure on the materials is gradually increased, the tones will be loud but wanting in distinctness, the galvanometer indicating interruptions; as the pressure is still increased, the tone becomes clearer, and the galvanometer will be stationary when a maximum of loudness and clearness is attained. If the pressure be further increased, the sounds become weaker though very clear; and as the pressure is still further augmented the sounds die out (as if the speaker were talking and walking away at the same time) until a point is arrived at where there is complete silence.

When the microphone is fixed to a resonant board, the lower contact should be fixed to the board, so that the sonorous vibrations act directly on it. The upper contact, where the pressure is applied, should be as free as possible from the influence of the vibrations, except those directly transmitted to it by the surfaces underneath; it (the upper surface) should have its inertia supplemented by that of a balanced weight. This inertia I find necessary to keep the contact unbroken by powerful vibrations. No spring can supply the required inertia; but an adjustable spring may be used to ensure that the comparatively heavy lever shall duly press on the contacts.

The superposed surfaces in contact may be screwed down by an insulated screw passing through them all, thus doing away with the lever and spring; but this arrangement is far more difficult to adjust, and the expansion by heat of the screw causes a varying pressure. It is exceedingly simple, however, easily made, and illustrates the theoretical conditions better than the balanced lever I have adopted in practice.

In order to study the theoretical considerations, and that with the most simple form of microphone freed from all surrounding mechanisms, let us take a flat piece of charcoal 2 millims. thick and 1 centim. square, and, after making electrical contact by means of a copper wire on the lower surface, glue that to a small resonant board or, better for the purpose of observation, to a block of wood 10 centims. square. Upon this superpose one or more similar blocks of charcoal, the upper surface in communication with a wire, the lowermost surface resting flat, or as nearly so as possible, on the lower block.



The required pressure is put on the upper block; and while in this state the two may be fastened together with glue at the sides, or, better, by an insulated screw. The pressure can then be removed, as the screw or glue equally preserves the force. Let the lower piece be called A and the upper B: when we subject this board to sonorous vibrations, we cannot imagine an undulatory movement of the actual wave-length in such a mass, that is a length comparable with the real wave-length of the sonorous wave, which may be several feet. Nor can we imagine a wave of any length without admitting that the force must be transmitted from molecule to molecule throughout the entire length: thus any portion of a wave, of which this block represents a fraction, must be in molecular activity. The lower portion of the charcoal A, being part of the block itself, has this molecular action throughout, transmitting it also to the upper block. How is it that the molecular action at the surfaces of A and B should so vary the conductivity or electrical resistance as to throw it into waves in the exact form of the sonorous vibrations? It cannot be because it throws up the upper portion, making an intermittent current, because the upper portion is fastened to the lower, and the galvanometer does not indicate any interruption of current whatever. It cannot be because the molecules arrange themselves in stratified lines, becoming more or less conductive, as then surfaces would not be required—that is, we should not require discontinuity between the blocks A and B; nor would the upper surface be thrown up if the pressure be removed, as sand is on a vibrating glass. The throwing-up of this upper piece B when pressure is removed proves that a blow, pressure, or upheaval of the lower portion takes place: that this takes place there cannot be any doubt, as the surface, considered alone (having no depth), could not bodily quit its mass. In fact, there must have been a movement to a certain depth; and I am inclined to believe, from numerous experiments, that the whole block increases and diminishes in size at all points, in the centre as well as the surface, exactly in accordance with the form of the sonorous wave. Confining our attention, however, to points on A and B, how can this increased molecular size or form produce a change in the electrical waves? This may happen in two ways:—*first*, by increased pressure on the upper surface, due to its enlargement; or, *second*, the molecules themselves, finding a certain resistance opposed to their upward movement, spread themselves, making innumerable fresh points of contact. Thus an undulatory current would appear to be produced by infinite change in the number of fresh contacts. I am inclined to believe that both actions occur: but the latter seems to me the true explanation; for if the first were alone true, we should have a far greater effect from metal powder, carbon, or some elastic conductor, such as metallized silk, than from gold or other hard unoxidizable matter; but as the best results as regards the human voice were obtained from two surfaces of solid gold, I am inclined to view with more favour the idea that an infinite variety of fresh contacts brought into play by the molecular pressure affords the true explanation. It has the advantage of being supported by the numerous forms of microphone I have constructed, in all of which I can fully trace the effect.

I have been very much struck by the great mechanical force exerted by this uprising of the molecules under sonorous vibrations. With vibrations from a musical box 2 feet in length, I found that one ounce of lead was not sufficient on a surface of contact 1 centim. square to maintain constant contact; and it was only by removing the musical box to a distance of several feet that I was enabled to preserve continuity of current with a moderate pressure. I have spoken to forty microphones at once; and they all seemed to respond with equal force. Of course there must be a loss of energy in the conversion of molecular vibrations into electrical waves; but it is so small that I have never been able to measure it with the simple appliances at my disposal. I have examined every portion of my room—wood, stone, metal, in fact all parts—and even a piece of india-rubber: all were in molecular movement whenever I spoke. As yet I have found no such insulator for sound as gutta-percha is for electricity. Caoutchouc seems to be the best; but I have never been able by the use of any amount at my disposal to prevent the microphone reporting all it heard.

The question of insulation has now become one of necessity, as the microphone has opened to us a world of sounds, of the existence of which we were unaware. If we can insulate the instrument so as to direct its powers on any single object, as at present I am able to do on a moving fly, it will be possible to investigate that object undisturbed by the pandemonium of sounds which at present the microphone reveals where we thought complete silence prevailed.

I have recently made the following curious observation:—A microphone on a resonant board is placed in a battery-circuit together with two telephones. When one of these is placed on the resonant board, a continuous sound will emanate from the other. The sound is started by the vibration which is imparted to the board when the telephone is placed on it; this impulse, passing through the microphone, sets both telephone-disks in motion; and the instrument on the board, reacting through the microphone, causes a continuous sound to be produced, which is permanent so long as the independent current of electricity is maintained through the microphone. It follows that the question of providing a *relay* for the human voice in telephony is thus solved.

The transmission of sound through the microphone is perfectly duplex; for if two correspondents use microphones as transmitters and telephones as receivers, each can hear the other, but his own speech is inaudible; and if each sing a different note, no chord is heard. The experiments on the deaf have proved that they can be made to hear the tick of a watch, but not, as yet, human speech distinctly; and my results in

Fig. 1.

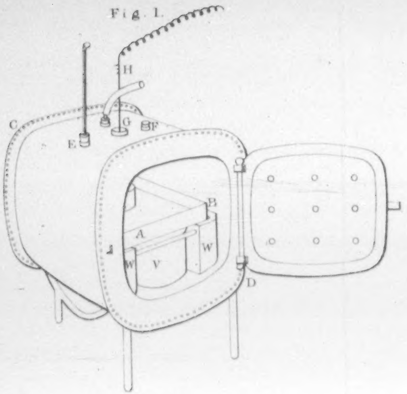

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Fig. 2.

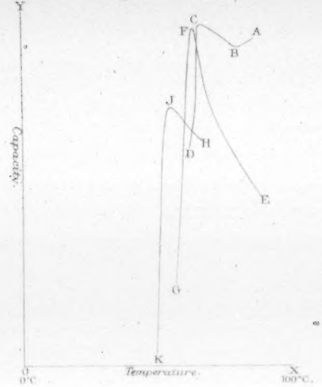


Fig. 3.

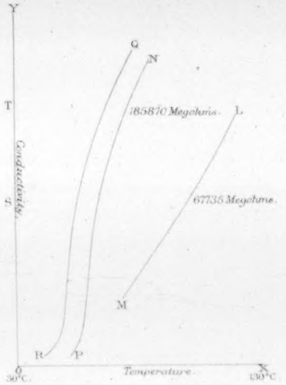


Fig. 4.

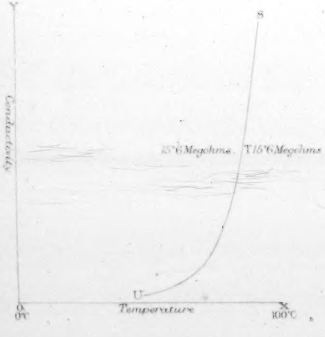


Fig. 5.

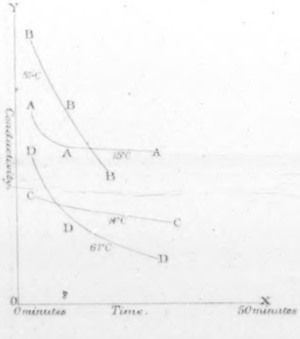


Fig. 6.

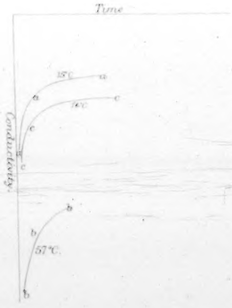
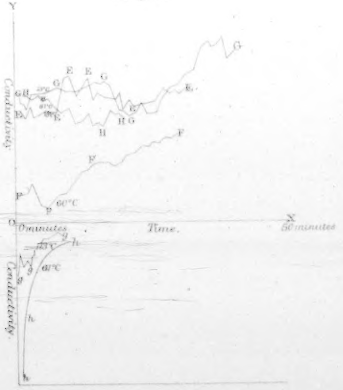


Fig. 7.



Mintern Bros lith.

this direction point to the conclusion that we only hear ourselves speak through the bones and not through the ears.

However simple the microphone may appear at first glance, it has taken me many months of unremitting labour and study to bring to its present state through the numerous forms each suitable for a special object. The field of usefulness for it widens every day. Sir Henry Thompson has succeeded in applying it to surgical operations of great delicacy; and by its means splinters, bullets, in fact all foreign matter, can be at once detected. Dr. Richardson and myself have been experimenting in lung- and heart-diseases; and although the application by Sir H. Thompson is more successful, I do not doubt that we shall ultimately succeed. There is also hope that deafness may be relieved. For telephony articulation has become perfect, and the loudness increased. Duplex and multiplex telegraphy will profit by its use; and there is hardly a science, where acoustics has any direct or indirect relation, which will not be benefited. And I feel happy in being able to present this paper on the results obtained by a purely physical action to such an appropriate and appreciative body as the Physical Society.

In conclusion, allow me to state that throughout the whole of my investigations I have used Prof. Bell's wonderfully sensitive telephone instrument as a receiver, and that it is owing to the discovery of so admirable an appliance that I have been enabled to commence and follow up my researches.

XXVIII. *On Brass Wind Instruments as Resonators.*

By D. J. Blaikley[*].

[Plate VI.]

In bringing before the Physical Society a few notes and experiments on this subject, I would desire to say that they are the result of an attempt to carry somewhat more into detail than, as far as I am aware, has hitherto been done, some acoustical investigations of the late Sir C. Wheatstone. A most interesting paper on Wheatstone's work in this field was brought before the Musical Association by Professor W. G. Adams in 1876; and to that paper I am in great measure indebted.

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[*] Read May 25, 1878.

A brass instrument may be defined as a resonator capable of reinforcing a certain fundamental periodic vibration originated by the lips, and all such vibrations as have for their relative numbers 2, 3, 4, &c. when the fundamental note is represented by unity,—these vibrational numbers being the basis of what is known as the natural harmonic series of musical intervals—and this series being the same, whatever may be the absolute pitch of the fundamental note or the character of tone of the instrument.

It is possible to make the lips give notes which, although scarcely audible, are of definite pitch, without the use of an instrument, just as a tuning-fork gives its proper note with or without a resonator.

There are two simple forms of resonators which give the series of notes required in wind instruments: these are the open tube of equal section throughout, and the cone complete to its apex, where it is of course closed. In the tube the wave-length of any note is inversely proportional to its vibrational number; and the nodes or points of maximum compression and rarefaction, and the centres of the ventral segments, or points of maximum amplitude of vibration are equidistant: but in the cone this is not the case. Wheatstone found experimentally that the notes of a closed cone agree in pitch with those of an open tube of the same length; and therefore the prime or fundamental tone of such a cone is an octave higher than the prime of a closed tube of the same length. He found also that in conic frustra of similar lengths, but of different proportions as regards the diameters of their ends, the pitch varied, rising as the difference between the two ends increased when the small end was closed, and becoming lower under the same conditions when the large end was closed. The accompanying diagram (Plate VI.) shows the positions of the nodes and centres of ventral segments in an open tube and a cone of the same length for the notes *c*, *c′*, *g′*, *c″*, marked 1, 2, 3, 4 (*c* having 128 vib., and a wave-length of 105 in. at 60° F.). The numerals grouped together and marked N show the positions of the nodal points or surfaces, and those marked $\frac{V.S}{2}$ the centres of the ventral segments or points of maximum vibration. The effect that the diminishing size of the cone has upon the position of the nodes may be easily traced. Whilst the positions of the centres of the ventral segments remain the same as in the open tube (the numerals for these on the cone in the diagram falling exactly under those for the open tube), the nodes are gradually further and further apart, dividing their respective ventral segments more and more unequally, until at the apex of the cone is a node common to all the notes. It follows from this that the centre of a ventral segment in a cone is not the centre of the length between its nodes, and, conversely, that as the diameters of the two ends of the ventral segment approach equality, so does the position of the node become more central, until the condition of vibration existing in an open cylindrical tube is reached; and such a tube may evidently be considered as a portion of a cone whose apex is at an infinite distance. It is to be noticed that in the cone the number of ¼ wave-lengths, or semi-ventral segments, is not directly proportional to the vibrational number as in the open tube, but, with the exception of the fundamental note, is always in excess. Thus let

N = number of ¼ wave-lengths,

n = relative vibrational number;

then

$$N = n + (n-1) = 2n - 1.$$

Instances.—Note 1 (fundamental) $N = 1 + (1-1) = 1$,

Note 4 (double octave) $N = 4 + (4-1) = 7$.

The velocity of the portion of wave or waves in the cone therefore differs with the pitch of the note, and is in no case the same as the velocity in free space. Assuming this latter to be 1120 feet per second, we should have in the cone the following velocities:—

Note.	*n.*	N.	Feet per second.
c 128	1	1	2240
c′ 256	2	3	1493·4
g′ 384	3	5	1344
c″ 512	4	7	1280

and the space traversed by the waves of the different notes in one second, measuring from the apex of the cone to, say, the ear of an observer:—

c 128	....	1122·1875 feet.
c′ 256	....	1121·0937 "
g′ 384	....	1120·7292 "
c″ 512	....	1120·5468 "

The method I used to find the positions of the nodal points in the cone, and which is applicable to wind instruments or tubes of any varying section, may be illustrated by a conic frustum open at both ends. Holding a vibrating fork over one end (in this case *c* 512), gradually sink the tube in water: the water-level when the tube is giving its maximum resonance shows the position of the node.

Brass instruments are generally considered to be cones, or cones combined with cylindrical tubing, neither of which descriptions properly applies; and this I will endeavour to make clear by experiment. We may, in the first place, consider whether the resonance of cones and tubing is influenced appreciably by the action of the lips; and it will be found that, whether the lips or a tuning-fork be used to excite the vibration, the pitch is the same. Two illustrations may be given—the first a common hunting-horn, pitch *c* 512 when it is blown, and giving an excellent resonance to the *c* 512 fork when the mouthpiece is closed; if, however, we slightly alter its length either way, the resonance to the fork is no longer at its maximum. For the second illustration, I take a cylindrical tube which becomes closed on being placed against the lips: blowing it as a wind instrument, we find its proper tones are *c* 128, *g′* 384, *e″* 640, *b″*♭ 896, &c., the same as it would give as a resonator, and that the pitch of these tones is so definite that it is very difficult to alter any of them by the lips more than two or three vibrations, except the lowest. We may here note that the power of a resonator to reinforce the different notes of a series of tones, with the prime or fundamental one of which it is not truly in unison, is much greater for the fundamental than for the higher notes; and this gives the reason for the ease with which the fundamental note of a wind instrument may be varied within pretty wide limits, say half a tone sharper or flatter than its proper pitch. Taking, for illustration, a closed tube 21 inches long, it will be found to give appreciable resonance to a fork of 128 vibrations with quarter wave-length of 26¼ inches, but scarcely any to a fork of 384 vibrations (*g′* the twelfth from *c* 128) with quarter wave-length of 8¾ inches: when the *c* fork is sounding, the length of the resonance-chamber is to the quarter wave-length as 21 to 26¼; but when the *g* fork is used, the corresponding proportion is practically as 3½ to 8¾; for in this case there is a second node at a half wave-length, or 17½ inches from the closed end.

For musical purposes a cylindrical tube blown by the lips is evidently unsuited, by reason of its poor tone, as well as by its giving only the odd intervals. The cone gives the required intervals; but it cannot be used by the lips in its complete form; it would be necessary to cut off a considerable portion to get sufficient width for the action of the lips. Assuming the cone shown on diagram to be cut at the second node of note 4 (counting the node at the apex as the first) and there closed by the lips, that note of the original cone can still be sounded, but no other; the other notes that can be produced may be regarded as the notes 3 and 2 made flatter by their nodes being drawn back, as it were, to the position of node 4, where the cone is cut and the lips are placed; the original notes 2, 3, 4, or *c′*, *g′*, *c″*, becoming thus the 1st, 2nd, and 3rd notes of a new inharmonic series, with pitches approximately *c*♯, *e*♭′, *c″*—thus approaching the notes of a cylindrical stopped tube. I have here two other tubes tapering in different degrees—the first two proper tones on the one being *c′* and *c*♯″, and on the other *c′* and *e″* (a major tenth). From these experiments it may be seen that, by using portions of cones of different proportions with their small ends closed, it is possible to get different series of intervals varying between those of an open and those of a closed cylindrical tube—that is, the first interval varying between an octave and a twelfth.

One of the examples just shown (the tube with notes *c′* and *c*♯″) appears to give intervals not very far removed from those required: it may be made use of to illustrate the effect of the combination of a cone with cylindrical tubing, such tubing being of necessity used in practice in connexion with valves or slides to complete the scale. Flattening this cone a fourth, from *c′* to *g*, by adding tube, it gives the intervals *g*, *e′*, *d″* in place of the g, g', d'' required, or the ratios 1, $1\frac{2}{3}$, 3 in place of 1, 2, 3, the second interval being actually greater than the first.

These illustrations prove that neither a conic frustum, nor a conic frustum combined with cylindrical tubing, can truly be resonators to notes in the natural harmonic series; but seeing that a bugle or other wind instrument, although it has a considerable diameter at the mouthpiece, may nevertheless be in tune, it appears that its nodal points cannot be in the same positions as those in the cone. On the diagram is represented a bugle of the same pitch as the open tube and cone, with the positions of its nodes and semi- ventral segments as determined by experiment with tuning-forks. Comparing on the diagram the positions of the nodes of any given note in both the bugle and the cone, it will be noticed that there are great differences. The nodes of note 2 show this clearly. Compare lengths from both ends: from mouthpiece to node the length is more nearly equal to that between similar nodes on cylindrical tubing than to that between similar nodes on the cone; but from node to open end it is greater than on the cone, the bugle opening more rapidly.

Thus, then, by altering the proportions of the different semi-ventral segments of which such an instrument may be conceived to be built up, the positions of the nodes may be so arranged that there shall be a node for every note of the harmonic series at the mouthpiece as required; and according as that is more or less perfectly effected will the instrument be more or less perfectly in tune. This bugle is divided into its seven semi- ventral segments for its 4th note, *c* 512, according to the diagram; and it will be found that by blowing at any one of the nodal points, with any length of the bugle containing an odd number of semi- ventral segments, the note c'' can be produced. The total number of pieces and combinations that can give this note is eighteen.

Having given these few illustrations of the conditions upon which correct intonation, or the relative pitch of the different notes that can be sounded on a brass instrument, depends, I will now endeavour to show the connexion there is between this point and the question of quality of tone, understanding by quality of tone that characteristic of sound which enables us to recognize a difference between tones of the same pitch. Helmholtz has fully demonstrated that it is only in exceptional cases that we hear a simple musical tone—the vast majority of musical tones being in reality compound tones, in which the fundamental or prime tone has blended with it many upper partial tones of the natural harmonic series,—and that the variety of quality of tone depends mainly upon the number and intensity of these upper partial tones. Blowing the note *c* 256 on three resonators of different forms we get three distinctly different qualities of tone: the resonators now used are a common paraffin-lamp chimney, the conic frustum already shown (having for its first two proper tones c' and $c''\sharp$), and the bugle. Analyzing these three tones by tuning-forks or resonators, we find that the lamp-chimney of irregular form gives no upper partials; the tone is pure or simple. The cone has the second and third partials sounding, but not strongly, as it is not strictly in tune for them, or, in other words, there is a difference of phase between the prime tone and the partials. And the bugle has all the partials up to the seventh, gradually diminishing in power, but all tolerably strong up to the fifth inclusive. Slightly altering the form of the cone by adding tubing to the narrow end, and maintaining the original pitch of the prime tone (*c* 256), by cutting a portion off the wide end the pitch of the second tone may be altered until it is *c* 512, an exact octave from the prime; and we find that the quality of tone of the prime or fundamental note is altered, owing to the more perfect resonance which the cone now gives to its second partial. In its original form, with proper tones c'–$c\sharp''$, the cone could give but an imperfect resonance to c'', the second partial to its prime c'.

In the trombone and the euphonion we have two instruments of very different and characteristic qualities of tones—the trombone being brilliant and piercing, and the euphonion mellow. We may take the B♭ of about 120 vibrations (army pitch) on each of these and endeavour to give a visible proof of the existence of high upper partial tones. For this purpose I use small tubular resonators covered at one end with a tightly strained diaphragm or tympanum of goldbeater's skin, against the centre of which is hung a very small bead, or drop of sealing-wax, by means of a single thread of cocoon-silk. The two resonators now used are tuned respectively to the fourth and ninth partials of B♭, or *b'*♭ of 480 vibrations and *c'''* of 1024. When the proper tone of such a resonator is sounded in its neighbourhood, either as a simple tone or as a partial in a compound tone, the agitation of the membrane puts the bead in violent motion, which can easily be seen in the image thrown on the screen by the electric lamp. It will be noticed that when B♭ is sounded, either on the euphonion or on the trombone, both resonators are agitated—but that the excursions of the bead due to the partial tone of 1024 vibrations are much greater with the latter than with the former instrument, although both are played with but moderate force, thus proving that, though partials as high as the ninth exist in the quality of tone produced by both these instruments, yet in the trombone the upper partials have much greater strength than in the euphonion. With a resonator more suitable for private experiment than these, I have distinctly heard the sixteenth partial tone in the B♭ of the trombone. A tapering tube open at both ends, or a common wine-bottle with the bottom knocked out, is very convenient for analyzing tones. Sinking such a tube in water and holding the ear close against the small end, the various partials existing in a given compound tone may be readily discerned, as the length of the tube changes according to the depth it is immersed in the water.

Although one wind instrument may be made to approach another in quality of tone by means of different methods of blowing, and it is therefore not so easy to analyze the tones of these as it is those of keyed instruments with fixed tones, yet I have endeavoured to establish some general data; and these I will lay before you. The instruments the tones of which I have analyzed are the B♭ tenor trombone, the B♭ euphonion, the F French horn, the B♭ cornet, and the bugle. The partial tones named in the Table are those heard when the instruments are gently blown; with loud blowing higher tones can be discerned. The ordinary marks of musical expression, *pp*, *p*, *mf*, *f*, are added in cases where I found it possible to make a comparison.

Instrument.	Note.	No. of vibrations.	Partial tones heard.
B♭ Trombone ...	B,♭	60	1, 2, 3, 4, 5, 6, &c. to 16. *p*
	B♭	120	1, 2, 3, 4, 5, 6, &c. to 12. *p*
	f	180	1, 2, 3, 4, 5, 6, 7. *p*
B♭ Euphonion ...	B,♭	60	1, 2, 3, 4, 5, 6, &c. to 12; higher [than 12 weak. *p*
	B♭	120	1, 2, 3, 4, 5, 6, 7. *f mf p*
	f	180	1, 2, 3, 4, 5. *p*
F French horn ...	*c*	135	1, 2, 3, 4, 5, 6, 7, 8. *mf p pp*
	f	180	1, 2, 3, 4, 5, 6. *mf p*
	f	360	1, 2, 3, 4, 5, 6. *p p*
B♭ Cornet...........	*b*♭	240	1, 2, 3, 4, 5, 6, 7, 8. *f f p p*
Bugle......	...	256	1, 2, 3, 4, 5, 6, 7. *f mf p pp*

While submitting that the different qualities of tone are accounted for by the difference in the number and force of the upper partials in any given compound tone, I must at the same time acknowledge that I can do no more than throw out a few suggestions with respect to the causes that influence the production of such upper partials in this remarkable manner. The partials being in the natural harmonic series, it is evident that if the various proper tones of a vibrating column of air such as is enclosed in a wind instrument are not in exact agreement with this series, the resonance to the partials cannot be at its best. Take for illustration two instruments nominally the same (say two bugles), but with somewhat different qualities of tone. Suppose that a certain compound tone on both should have its first and second partials of equal intensity, but that one instrument has that one of its proper tones that is nearest in pitch to the required second partial a semitone sharper than that partial; the supposed compound tone sounded on that instrument will be deficient in the quality the second partial should give.

As regards instruments of different characters, the chief points influencing the tone are the general form of the instrument (understanding by this the proportions of the column of air, and not the shape into which the instrument may be bent up for the convenience of the player), the extent of the flanging of the bell, and the form of the mouthpiece. As an illustration of the first of these conditions the trombone may be compared with the euphonion; the tubing of the trombone is cylindrical for about two thirds of its length from the mouthpiece, but the euphonion opens with gradually increasing curvature from the mouthpiece to the rim of the bell. The high upper partials being more powerful on the former than on the latter instrument, it would appear that the cylindrical tubing has the power of maintaining the intensity of the short waves to a greater extent than the tapering tubing has. The bell-flange may be increased in size to a considerable degree without altering the pitch of an instrument; but such increase has a marked effect on the quality of tone, greatly subduing the force of the upper partials. I find by experiment that the pitch is not altered by the extension of the flange curvature beyond a point at which its tangent would make an angle of about 40° with the axis of the instrument, although the quality of tone is decidedly altered by such extension. This may be illustrated by changing the bell-end of a bugle for a bell with much wider flange, more like that of a French horn: comparing the two, it will be noticed that the change in quality of tone is very marked.

The form of the cup of the mouthpiece varies for different instruments, from that of a long deep conical funnel to that of a comparatively shallow well-rounded cup—the first form representing the French-horn mouthpiece, and the second the mouthpiece for instruments of brilliant tone, as the trumpet and trombone; those for cornets, bugles, and saxhorns are of an intermediate character. Although it is manifest that a shallow cupped mouthpiece favours the production of high upper partials, I have not as yet succeeded in arranging any experiments which would illustrate the cause of this. One fact, however, noticed by many observers, appears to me to be suggestive, and worth bearing in mind in connexion with this subject. It is this:—If a vibrating tuning-fork be placed on a sounding-board, the quality of tone it gives varies with the pressure applied: touching the board very lightly with the fork the prime tone is well heard; but on pressing the fork down to the board the tone appears to jump up an octave; at least the second partial (octave of the prime) is heard with great distinctness. This experiment appears to prove that if an elastic resonant body (in this case the resonant board) is in a state of initial pressure at the point of origin of vibrations, a vibration that would otherwise be simply pendular becomes a vibration compounded of two or more simple pendular vibrations. Applying this consideration to wind instruments, and bearing in mind the initial pressure caused by the escape of air from the lips, it would appear probable that mouthpieces of different forms so modify this initial pressure as to cause a variety in the number and intensity of the upper partial tones.

XXIX. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

[Continued from p. 102.]

VI.

Further Examples of Cryohydrates and Cryogens.

§ 167. *Hydrate of Barium.*—On cooling a saturated solution of this salt, the well-known recognizable crystals are continually deposited until the temperature reaches $-0^\circ{\cdot}5$. At this temperature the cryohydrate is formed, the temperature remaining constant until solidification is complete. The barium was estimated by adding carbonate of ammonium and gently igniting.

grams.		$BaO\,CO_2$.		BaO.		BaO per cent.
22·1204	gave	0·4271	or	0·331707	or	1·4995
19·6436	„	0·3790	„	0·29435	„	1·4984
14·7921	„	0·2924	„	0·22709	„	1·5352

The above analyses are of three separate liquid residues after the separation of two crops of cryohydrate in each case.

The water-worth calculated on the whole three of these results is 565.

As a cryogen the same temperature $(-0^\circ{\cdot}5)$ was obtained.

§ 168. *Hydrate of Strontium.*—On lowering the temperature of a saturated solution of this hydrate, crystals of the same separated until the temperature −0°·1 was reached; the cryohydrate then formed.

grams.		$SrO\,CO_2$.		SrO.		SrO per cent.
17·2620	gave	0·0944	or	0·5468	or	0·3838
13·5124	„	0·0774	„	0·5728	„	0·4020

The analyses were of different liquid residues after two crops of cryohydrate had been separated from each. The water-worth derived from the mean of these two analyses appears to be 1463. As cryogens, $SrO\,H_2O$ or SrO when mixed with ice did not lower the temperature below 0°. A very slight fall to −0°·09 was obtained on slaking SrO with water and allowing it to assume the normal temperature before mixing with ice. Such a fall, however, can scarcely be recognized.

§ 169. *Hydrate of Calcium.*—This body, as is well known, presents the very interesting peculiarity of being more soluble in cold than in hot water. On further cooling the solution saturated at a certain temperature above 0°, one gets an imperfectly saturated solution; and on still further cooling, ice appears. But if the solution be kept saturated during cooling, which can be well effected by continued stirring with some hydrate precipitated by rise of temperature in another quantity, the cryohydrate appears at −0°·15.

grams.		$CaO\,CO_2$.		CaO.		CaO per cent.
22·1094	gave	0·1030	or	0·057630	or	0·26
23·3498	„	0·1222	„	0·068432	„	0·29

The analyses were of different liquid residues after two crops of cryohydrate had separated: the mean of these two results corresponds to the relation

$$CaO + 1116 H_2 C,$$

Employed as a cryogen, −0°·18 was the lowest temperature reached. The only data I can find of the solubility of lime at different temperatures are those of Dalton; from whose experiments it appeared that lime-water saturated at

100° C.	contains	0·1050	per cent. of	$CaO\,H_2O$
54·4	”	0·1371	”	”
15·5	”	0·1712	”	”

From my results it appears that, the mean CaO being 0·275 per cent. (the mean of two analyses of the cryohydrate at −0°·15 gave 0·3634 per cent. of $CaO\,H_2O$), lime is 3½ times more soluble in water at −0°·15 C. than at 100 C.

With regard to these water-worths,

	W.W.
Hydrate of barium	565
„ strontium . . .	1463
„ calcium	1116

it is not only noteworthy, but imperatively demands notice, that here calcium lies between barium and strontium. They who are engaged with the spectra of these metals will scarcely need a further hint.

The melted cryohydrates of $SrO\,H_2O$ and $CaO\,H_2O$, which had been solidified in an ice and NaCl freezing-mixture, did not exhibit the characteristic opacity of cryohydrates. They became milky in a carbonic acid and ether cryogen, but did not seem even then to assume the characteristic opacity. A trace of this true opacity appeared with $BaO\,H_2O$.

§ 170. *Hydrate of Potassium.*—A concentrated solution, namely a solution resulting from the deliquescence of the solid hydrate in moist air free from carbonic acid, did not solidify on being subjected to a cryogen of CO_2 and ether: it, however, became syrupy. A dilute solution (indefinite) solidified wholly within the range of an ice-and-NaCl cryogen. The solid was transparent and resembled ice; it sank in water at 0° C.

As a cryogen, caustic potash gave a temperature of −19°·2 C. But, as will appear subsequently (and this is an important point), a salt which evolves heat on mixing with water makes a more powerful cryogen with ice if previously cooled; not so those which do not.

§ 171. *Permanganate of Potassium.*—On cooling a saturated solution of this salt, crystals of the permanganate separated out down to 0° C. The cryohydrate was formed at −0°·57; and the temperature then ceased to sink. The estimation of the water was by evaporation at 100°. The samples are from different preparations. In each case several crops of the solid cryohydrate had been removed.

grams.	Anhydrous salt.	Per cent.
20·4624	0·5874	2·871
19·6134	0·5910	3·013
19·7115	0·5249	2·663
19·7476	0·5318	2·693
12·6320	0·3718	2·943

The mean of these rather discordant results shows a water-worth of 608·3 ($K_2 MnO_8$).

As a cryogen, permanganate of potash gives a temperature of $-0^{\circ}{\cdot}52$.

§ 172. *Acetate of Lead.*—The cryohydrate of acetate of lead forms at $-1^{\circ}{\cdot}4$ C. After the separation of several crops, in each case the residual liquids, after weighing, were repeatedly evaporated with an excess of nitric acid and gently heated. It is found that the acetate is thereby completely converted into the nitrate.

grams.		Nitrate.		Per cent. of acetate.
14·8195	gave	2·7906	=	18·4
6·9029	„	1·2401	=	17·5
7·4904	„	1·3700	=	18·0

The water-worth, calculated on the mean of these three results, is 82·3. The temperature of the acetate-of-lead cryogen is $-1^{\circ}{\cdot}7$.

§ 173. *Sulphate of Zinc and Potassium.*—The cryohydrate forms at $-1^{\circ}{\cdot}25$. The analyses are, as before, of different residual liquids. The liquid cryohydrate was evaporated to dryness at 100° and heated to incipient fusion.

grams.		$ZnSO_4 + K_2 SO_4$.		Per cent.
9·1020	yielded	0·7274	or	7·992
9·0934	„	0·7739	„	8·510

The mean of these results gives the water-worth 167·4. As a cryogen, the same double salt gives $-1^{\circ}{\cdot}01$. The temperature of solidification of this cryohydrate and the percentage of salt it contains are approximately those of $K_2 SO_4$, its least-soluble constituent (see §§ 22, 71).

	Temperature of cryohydrate.	Per cent. of salt.
$K_2 SO_4$	$-1^{\circ}{\cdot}5$	7·8
$ZnSO_4$	-7°	30·84
$K_2 SO_4 + ZnSO_4$	$-1^{\circ}{\cdot}25$	8·25

Comparing this fact with those developed in §§ 109–120, where mixtures of salts were employed, we find that while with such mixtures the more powerful cryogen governs the temperature, here it is the less powerful cryogen which does so.

§ 174. *Ferrocyanide of Potassium*—The cryohydrate of this salt forms at −1°·7. Two analyses of the same residual liquid were made by evaporating at 100°, and subsequent stirring with free exposure to the air at the same temperature.

grams.		K_4FeCy_6.		Per cent.
6·6510	gave	0·7987	or	12
6·5080	„	0·7665	„	11·8

The mean indicates the formula

$$K_4FeCy_6 + 151{\cdot}6\,H_2O.$$

The temperature of the cryogen is −1°·61. If this body had been the first to be experimented on in the direction which has led to the discovery of the cryohydrates, it is possible that the whole class might have escaped notice, because, when the cryohydrate is allowed to melt, a considerable quantity of yellow salt (terhydrate or subcryohydrate) falls down unless the liquid is kept well agitated. Though not peculiar to this salt, it is perhaps more marked with it than with any other. To be viewed almost as a corollary to the above fact is the following one concerning the same salt. When a solution of the strength of the cryohydrate is cooled, there may be a simultaneous formation of ice and some hydrated or anhydrous ferrocyanide: the one floats; the other sinks. As before pointed out in other cases, this independent separation of the constituents of the cryohydrate is entirely prevented by placing in the solution a fragment of previously formed cayohydrate.

§ 175. *Ferricyanide of Potassium.*—At a temperature of −3°·9 a saturated solution of this salt began to give up its cryohydrate, having previously given up a less hydrated salt. Though several determinations of the amount of salt in the residual liquid were made both by evaporation over a water-bath and drying *in vacuo* over sulphuric acid, the results differed from one another by several per cent. The lowest was 19·8 per cent., the highest 24 per cent. The temperature of the cryogen is −3°·9 C. The ambiguity in the amount of water in the cryohydrate finds its counterpart in the similar ambiguity in the water of crystallization of the ordinary salt.

§ 176. *Nitrate of Urea.*—The cryohydrate first appears at −4°, on cooling a saturated solution. The residual liquids from two preparations, after about the same quantity of cryohydrate had separated, were very gently evaporated on a water-bath only just to complete dryness. If the substance be further heated, minute iridescent crystals begin to appear at that part of the residue where the basin is in contact with the bath. As soon as these began to appear the further heating was stopped.

grams.		Nitrate.		Per cent.
6·6889	gave	0·5693	or	8·64
6·7616	„	0·5844	„	8·51

The water-worth is accordingly 72·83. As a cryogen the temperature of −4°·5 is obtained.

§ 177. *Oxalate of Potassium.*—The temperature at which the cryohydrate formed was found to be −6° 3. On evaporating 3·2862 grams in a platinum capsule, igniting, and quickly cooling on a metal slab, 0·5790 of the carbonate was obtained (=17·62 per cent.).

In another analysis, 3·1500 grams, on evaporation to dryness on a water-bath, gave 0·6684 oxalate (21·22 per cent.). This gave on ignition 0·5531 of carbonate (17·56 per cent.), which by treatment with hydrochloric acid gave 0·5958 of chloride of potassium (18·88 per cent.). The percentage of carbonate agrees closely with that of the first analysis. The percentage of chloride differs only by 0·07 from that required on the conversion of 17·56 of carbonate. Hence it would seem that with due care oxalate of potassium may safely be estimated as carbonate, notwithstanding the hygroscopic character of the latter salt. It also appears (contrary to statements sometimes made) that oxalate of potassium does not retain any of its water of crystallization when its solution is evaporated to dryness at 100° C.; for the 17·56 per cent. of carbonate obtained is equivalent to 21·12 per cent. of oxalate, which only differs by 0·1 per cent. from 21·22, which was found. The water-worth (deduced from the chloride of potassium) is 17·3.

The temperature of the cryogen is −6°·2.

§ 178. *Fluoride of Sodium.*—This salt, like several other salts of sodium, is troublesome when attacked from the side of saturated solutions, because there appears to be a subcryohydrate. This salt also exhibits the very rare property of being almost equally soluble at all temperatures between 100° and −3°·9. On cooling a hot saturated solution to −2°, nothing separates. Between −2° and −4° an ice-like body is formed. The true cryohydrate appears to be formed at −5°·63; for this temperature is preserved till the whole is solid and opaque. Fluoride of sodium, as a cryogen, gives −3°·2. The cryohydrate has not been further examined.

§ 179. *Cyanide of Mercury.*—A concentrated solution gave up the anhydrous salt until −0°·45 was reached; then the cryohydrate was formed. The amount of salt was determined by evaporation over sulphuric acid *in vacuo.*

grams.		Cyanide.			
3·8835	gave	0·2892	or	7·45	per cent.
5·0238	„	0·3738	or	7·44	„

This percentage exhibits the water-worth of 174. The same salt as a cryogen reaches the temperature −0°·6.

§ 180. *Acetate of Zinc.*—A boiling saturated solution was allowed to cool to the atmospheric temperature (+15°). The residual liquid was drained from the separated crystals and introduced, together with a few crystals, into a stoppered bottle. After keeping in ice for nine hours with frequent agitation, all sign of further crystallization ceased. The zinc was estimated by precipitation with carbonate of sodium. It was thus found that the strength at 0° was 23 per cent. This solution, when artificially cooled, yields fern-like crystals at −5°·9; these gradually became opaque, the opacity forming in a frond-like manner; the whole became dry at the above temperature. An analysis of the residual liquid, after two crops of cryohydrate, showed that the cryohydrate had sensibly the same composition as the solution saturated at 0° C.; for

grms. Oxide.
5·9980 gave 0·6103 or 23 per cent. anhydrous acetate.

§ 181. *Hyposulphite of Soda.*—The following are the temperatures at which solidification begins in solutions of varying strengths of this salt:—

TABLE XXXIX.

$N_2S_2O_3$, by weight.	Temperature, Centigrade.	Body found.
per cent.	°	
1	− 0·1	Ice.
2	− 0·4	"
3	− 0·65	"
5	− 1·2	"
6	− 1·5	Appearance of ice, but sinks in water at 0°. Perhaps due to interstitial solution. More probably a subcryohydrate.
10	− 2·5	
15	− 3·9	
20	− 5·45	
30	− 9·5 to −11·0	
30	−11	Cryohydrate.
33·5·5	0·0 (Kremers).	Ordinary hydrate.
41	+20	

A 30-per-cent. solution does not always give up a solid at −9°·5. Sometimes the temperature sinks to −12°·4; then the true cryohydrate is formed, and the temperature rises to −11° and remains constant till all is solid.

The solubilities at 0° and 20° are those given by Kremers. These and the determination for −11°, when plotted in the usual way, are found to lie on the same straight line. H. Schiff found at 19°·5 a saturated solution to contain 63·5 per cent. five-hydrated, or 45·8 per per cent. anhydrous salt. As a cryogen, the temperature −10° was reached.

§ 182. *Citric Acid.*—This body presented many difficulties; but as these difficulties occur again with most organic acids of high molecular weight, a special study was made of it. It is peculiarly liable in aqueous solution to supersaturation of the most persistent kind, especially when the solution is at a low temperature. At temperatures and under conditions which are capable of evolving the cryohydrate, the solution assumes sometimes an almost colloidal form, and shows no signs of eliminating solids unless other means besides mere lowering of temperature are employed.

From solutions ranging from 10 to 40 per cent. of anhydrous acid, ice is liberated; and this continues to 42·26 per cent., from which solution a cryohydrate separates at −9°·2. The following is a somewhat detailed account of the behaviour of solutions containing a greater percentage of acid than 40.

Two grams of a solution gave 0·8525 of citric acid, or 42·28 per cent. This gives a solid at −9°·2, which at first floats on the residual liquid. The solid consists of massive white agglomerated crystals. The crystals are hexagonal, but present rhomboidal elements, causing the edge of each crystal to be deeply and regularly serrate. When they melt, the rhomboidal crystals are themselves resolved into long slender prisms. A large quantity of such a solution retained its composition when nine tenths of it had been removed by solidification, nevertheless, if such a solution be kept perfectly still for many hours at −9°, a few ice spicula may be formed.

Other solutions, containing respectively 45, 45·9, 50, 50·7, and 51·5 per cent. of the anhydrous acid, were examined. It is only this latter which yields, on cooling, distinct quantities of the original salt: this it does at −6°, but only if a particle of the original salt be introduced and by diligent stirring. When undisturbed, this 51·5 solution may be cooled to −19°·5 without any solidification. So prone is this acid to exhibit supersaturation, that solutions both weaker and stronger than the 42·62 may be enriched on partial solidification. Thus a 50-per-cent. solution, though already stronger than the cryohydrate, may become still stronger by the separation of ice at −17°. There is therefore a large region of double supersaturation; the ice-curve crosses the acid or subcryohydrate-curve, both continuing their courses for an exceptionally long distance.

For the solubility at 0° C., a solution saturated above 0° C. was kept at 0° surrounded by ice and placed in an ice-safe for three days.

Solution.		Anhydrous acid.		Per cent.	Mean.
2·0962	gave	1·0755	or	51·30	=51·285.
2·1288	,,	1·0914	,,	51·27	

Crystallized citric acid when added to water has a considerable cooling effect. Thus

110·9 grams of crystallized acid at 20°·5 C., added to
89 ,, water at . . . 16°·5
lowered the temperature to . 2°·5;

while

51·5 grams of anhydrous acid cooled to 0° C. and added to
48·5 ,, water cooled to . . 0°
gave a temperature of . . −6°.

The chief results may be summarized in the following Table:—

TABLE XL.

Citric acid (anhydrous).

Anhydrous acid, per cent.	Temperature at which solidification begins.	Body formed.
10	− 1°·1	Ice.
20	− 2·8	,,
30	− 5	,,
40	− 8·5	,,
42·62	− 9·2	Cryohydrate.
45	−11·3	At these temperatures ordinary hydrate, subcryohydrate, or even ice may be formed.
45·93	−11·7	
47·06	−12·2	
50·7	−13·7	
51·5	−15	

As a cryogen, the lowest temperature attainable is −9°·3; and this confirms the composition of the cryohydrate which had been deduced synthetically. Neither cooling the acid to 0° C. nor cooling the two separately to −9° C. had any effect upon the temperature; but, of course, the more nearly the initial temperature is to the final one the less is the quantity of liquid formed.

Miscellaneous Notes.

§ 183. The following notes of salts which have not yet been fully examined may be useful.

Cyanide of Potassium, as a cryogen, gives a temperature of −21°·1. The cryohydrate forms at −33°, with a carbonic-acid and-ether cryogen. Compare § 170.

Oxalate of Sodium forms a cryohydrate at −1°·7 C.

Employed as cryogens, the following temperatures were obtained from the corresponding salts:—

Chloride of cadmium	− 8°·3 C.
,, nickel	−10·35
Citrate of sodium	−11·3
Acetate of calcium	−11·8
Chloride of cobalt	−15·35
,, manganese . . .	−28·0

Those of these bodies which evolve heat on mixture with water would, when cooled, depress the temperature more. Thus the chloride of manganese scarcely showed signs of a cryohydrate at −40° C.

Formate of Sodium, as a cryogen, gives −14°·3. A concentrated solution becomes semisolid at −14°, but does not become opaque or completely solid in a salt-ice cryogen (−22°).

Tannic Acid, as a cryogen, gives −1°·5.

Sulphurous Acid gives a cryohydrate at −1°·5.

Boracic Acid, as a cryogen, gives −0°·8. The cryohydrate forms at −0°·7.

Arsenious Acid.—The cryogen stands at −0°·3; the cryohydrate formed at −0°·5. Two samples of the melted and liquid cryohydrate were sealed hermetically. After two or three days it was found that a considerable quantity of a fine white powder had exhibited itself.

On the Separation of Water from Crystalline Solids, in Currents of Dry Air.

§ 184. The high water-worth of many of the cryohydrates (§ 88), and the want of evidence of simple arithmetical relationship between the atomic numbers of the water and salt of almost all these bodies, invited me to reexamine a few of the most definite and stable crystalline salts containing water And this invitation was the more pressing because, in the matter of the determination of water of crystallization, analysts have for the most part allowed themselves a far greater latitude in respect to agreement between the experiment made and the conclusion drawn than they have been willing to admit in regard to the other constituents of the salt. Prominent in respect to agreement between experiment and the derived constitution are the investigations of Graham, especially on the water of crystallization of single and double sulphates. Such accord is so rare, that in a very great many instances the experiments actually point to a different water-worth than that adopted by the experimenter.

That heat is sometimes liberated and sometimes absorbed when a salt is brought into contact with water, not only according to the nature of the anhydrous constituents, but also to the degree of hydration, has long since shown that there is some essential difference in the tension of the union which is established between the water on the one hand, and the more or less hydrated anhydride on the other. But the statements as to the conditions under which a salt becomes anhydrous, or exists in combination with a definite relative number of molecules of water, are neither definite nor satisfactory. The statement that a salt gives up *n* molecules of water when heated to the temperature E is inexact, (1) unless the hygrometric state of the air is given, (2) unless it is known whether free circulation takes place, and (3) unless the pressure on the salt is known. The statement that a salt gives up *m* molecules of water *in vacuo* (over a desiccator) is also ambiguous, in so far as it ignores the temperature.

The salt which I first examined in this respect was chloride of barium, $BaCl_2 + 2H_2O$ ($BaCl + 2HO$), it being a salt easily got quite pure and of a stable nature. The "pure" salt of commmerce was recrystallized, boiled with carbonate of barium, filtered and precipitated, and washed with alcohol. It was then twice recrystallized. It was then finely powdered, and a part A was dried for forty-eight hours in a good vacuum at a temperature of about 17° C.; a part B was dried between repeatedly renewed bibulous paper in a screw-press for the same time. Two analyses of each were made, the elements being estimated in the usual way.

Estimation of Barium.

	Weight of substance.	Sulphate.	Barium.	Per cent. of barium.
A (1) . .	2·7768	2·6912	1·57061	56·563
A (2) . .	1·3997	1·3406	0·78825	56·560
B (1) . .	1·3942	1·3445	0·79054	56·703
B (2) . .	0·8847	0·8480	0·49857	56·360

Estimation of Chlorine.

	Weight of substance.	Chloride of silver.	Chlorine.	Per cent. of chlorine.
A (1) . .	0·6579	0·7640	0·18900	28·72
A (2) . .	0·8559	0·9970	0·24665	28·70
B (1) . .	0·8849	1·0344	0·25590	28·92
B (2) . .	1·3965	1·6344	0·40433	28·91

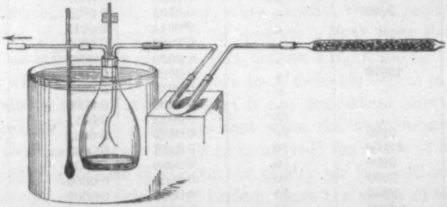
(Ba = 137, Ag = 108, S = 32, O = 16, Cl = 35·5).

Hence

	Calculated.	Dried *in vacuo.* Mean.	Dried between paper. Mean.
Ba . .	56·139	56·561	56·531
Cl_2 . .	29·098	28·912	28·710
$2H_2O$ . .	14·754	14·527	14·795
	100·000	100·000	100·000

From these analyses, and from the direction of their divergence from the theoretical composition of the salt, there can be no doubt about the composition of the salt; nor is there any doubt that the water is present in simple molecular ratio. Accordingly the hydrated chloride of barium is admirably adapted for examination as to the conditions under which it gives up water. The only statement I can find in this respect is that the hydrated salt gives up the whole of its water at 100° C.

§ 185. A two-ounce flask with the lip cut off was provided with a glass cap for use alone in the balance-case: the figure explains the rest. A given volume of air (measured by the quantity of water leaving the gasometer) is drawn in a given time over a thin layer of the hydrated salt, while the latter is heated to a given temperature. The air passes first through a long tube containing fragments of hydrate of potassium, and then through a tube containing glass and sulphuric acid.



As the flask had to be left for half an hour in the balance-case every time before weighing, the above experiments occupied a few weeks. At the end of this time the flask was found to have lost 0·0017 gram.

TABLE XLI.

Substance = 4·1605.

Volume of air drawn through flask at uniform rate of 3300 cubic centims. in 60 minutes.	Temperature.	Loss.	Loss by 3300 cubic centims.
cub. cent. 26400	17°	0·0008	0 0001
3300	25	0·0000	0·0000
"	40	0·0063	0·0063
"	"	0·0073	0·0073
"	"	0·0078	0·0078
"	"	0·0075	0·0075
"	"	0·0075	0·0075
"	"	0·0071	0·0071
"	"	0·0052	0·0052 (in 45′)
"	"	0·0078	0·0078
"	"	0·0066	0·0066
"	"	0·0062	0·0062
"	"	0·0044	0·0044 (in 30′)
"	"	0·0060	0·0060
19800	"	0·0412	0·0069
"	"	0·0420	0·0070
"	"	0·0346	0·0058
"	"	0·0407	0·0068
"	"	0·0340	0·0057
9900	"	0·0105	0·0035
"	"	0·0044	0·0015
"	"	0·0022	0·0007
"	"	0·0020	0·0007
19800	"	0·0029	0·0005
"	"	0·0059	0·0009
"	"	0·0000	0·0000
"	60	0·0063	0·0011
9900	70	0·0099	0·0033
19800	70	0·0256	0·0043
9900	70	0·0090	0·0030
9900	50	0·0000	0·0000
9900	50	0·0000	0·0000
9900	60	0·0038	0·0013
19800	70	0·0210	0·0035
9900	55	0·0000	0·0000
9900	58	0·0000	0·0000
9900	59	0·0000	0·0000
9900	60	0·0038	0·0013
19800	70	0·0187	0·0031
26400	70	0·0259	0·0032
39600	70	0·0411	0·0034
9900	80	0·0239	0·0080
9900	90	0·0483	0·0161
9900	90	0·0358	0·0119
9900	80	0·0151	0·0050
9900	80	0·0182	0·0061
9900	60	0·0010	0·0003
9900	90	0·0021	0·0007
6600	100	0·0000	0·0000

Examining the final result as a direct determination of the whole of the water, I found that the 4·1605 grams had lost 0·6087 gram, or 14·63 per cent., instead of the theoretical amount 14·75.

The actual weight of water which a given weight of the salt lost at a given temperature in a given time has little interest, because it is conditioned by the attitude of the salt to the air-current in the flask, and it is also governed by the rate. But points of very great interest are nevertheless presented when the above numbers are compared. The first loss, at 17° C., may probably be attributable to the more complete drying of the salt, since no further loss was experienced at 25°. Starting at 40°, a considerable loss was experienced, which continued with very considerable regularity until the residue approached in composition to the one-atom hydrate $BaCl_2 + H_2O$; the loss then suddenly diminished and abruptly stopped. The total loss experienced by the 4·1605 grams of salt when this point was reached is 0·3009—that is, 7·21 per cent. As the percentage of water in $BaCl_2 + H_2O$ is 7·37, there can be no question that there is a difference in the strength of union of the two water molecules to the salt, or, more exactly, that it requires different physical conditions to separate αH_2O from $BaCl_2$ than are sufficient to separate βH_2O from $\alpha H_2O, BaCl_2$.

At what minimum temperature the β molecule begins to be separated is missed in this Table: it lies somewhere between 25° and 40°. But it appears that when the temperature is such that one molecule begins to be stirred, the whole of that molecule is removed if the current of dry air be continued. In the case of the chloride of barium, there is a range of temperature below 60° and reaching down to the above-mentioned minimum, in which the α molecule is fixed while the β molecule is removable.

The minimum temperature required to disconnect the α molecule is well marked. The salt having ceased to lose weight at 40° C., lost weight distinctly at 60°, and still more rapidly at 70°. On reducing the temperature to 50° no loss could be detected; at 60° the same as before, and at 70° the same as before. At 55° there was no loss, nor at 58°, nor at 59°; but at 60° the original loss was reestablished. And until the salt is becoming anhydrous, for each temperature there is a pretty constant loss.

The anhydrous $BaCl_2$ thus obtained, when mixed with water, may raise the temperature from 19° to 38°. The solution is perfectly limpid and neutral.

§ 186. In order to make a more systematic attack on the β molecule, a fresh quantity was taken of the salt which had been dried *in vacuo* over sulphuric acid, and had then stood in air over sulphuric acid for three weeks.

TABLE XLII.

Substance = 5·6462.

Volume of air drawn through at uniform rate of 3300 cubic centims. in 15′.	Temperature.	Loss.	Loss by 3300 cubic centims.
9900	26°	0·0005	·0002
"	29	0·0012	·0004
"	32	0·0025	·0008
"	34	0·0053	·0018
"	36	0·0068	·0023
"	38	0·0089	·0030
"	40	0·0129	·0043
"	50	0·0236	·0079
16500	58	0·1450	·0290
9900	53	0·0446	·0149
"	50	0·0222	·0074
"	45	0·0209	·0070 (in 30′)
19800	55·5	0·0821	·0137
"	"	0·0192	·0032
9900	"	0·0022	·0007
6600	"	0·0014	·0007
19800	56	0·0074	·0012
9900	57	0·0029	·0010
"	57	0·0022	·0007
19800	57	0·0000	·0000

It seems that the almost inappreciable loss at 26° is really continuous with the greater losses at higher temperatures. The loss at 25° having been shown in Table XLI. to be inappreciable, we may consider the loss to begin between 25° and 26°. It is observed that the rate in Table XLII. is four times as great as in Table XLI.; and a consequence of this is that, for given volumes at the same temperature (40°), the losses are absolutely and relatively to the quantity less in Table XLII. than in Table XLI., but not four times as small. Hence, as we might anticipate, at a given temperature and for a given volume more water is withdrawn by a slow current than by a quick one; while in a given time more water is withdrawn by a quick current than by a slow one. With regard to the first of these facts, it need only be remembered that the slow current becomes more saturated than the quick one. Although the cessation of loss is for both atoms sufficiently well marked and abrupt, the final balance of water is retained in both cases with considerable tenacity.

In the second series of experiments the flask preserved its weight exactly. The total loss on the 5·6462 grams was 0·4119 gram, showing a percentage loss of 7·277.

The whole analysis now stands as follows, allowing for the loss of the glass in the first series, for the salt dried over sulphuric acid:—

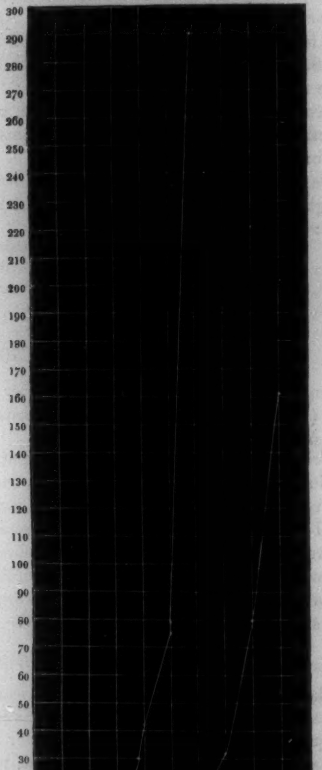
			Calculated.
Ba	56·56		56·14
Cl_2	28·91		29·10
αH_2O	7·44		14·76
βH_2O	7·23	(7·28 and 7·19)	
	100·14		100·00

On mixing the body $BaCl_2 + H_2O$ with water a rise from 21° to 27° (or 6°) was obtained. The anhydrous salt with water gave from 19° to 38° (or 19°).

§ 187. Briefly to recapitulate concerning $BaCl_2 + 2H_2O$. At the ordinary barometric pressure, and in a current of air dried and freed from carbonic acid, one water molecule is removed at all temperatures above 25° C., the other at all temperatures above 60° C. In the figure (p. 112) A shows the rates of loss of the β molecule in tenths of milligrams, the ordinates being proportional to such losses. The abscissæ are the temperatures. B shows the losses in like manner of the α molecule.

Chromatic Value of other Media than Water.

§ 188. There are few media besides water which dissolve metallic salts. Amongst the few glycerine stands preeminent; and this liquid is indeed comparable with water itself in its solvent power. On account of this very solvent power, there appears to be at present no evidence of the replacement of water by glycerine in solid hydrated salts, similar to the replacement in siliceous jellies. Some glycerates (using the term homologously with hydrates) are well-defined bodies enough; and the properties of some new ones will be described subsequently. Here I shall confine myself to the description of the effect upon



the colours of a few salt solutions, according as the solvent is water or glycerine. Being partially what is called "colour-blind," I have, of course, availed myself of the services of my friends in describing the appearances presented.

§ 189. Many are entertaining the idea of the relationship between the vibrating periods of the light-wave and the mass of the molecule, simple or compound, of the medium. The expression "loading" a molecule, by associating it with another more or less massive molecule, may perhaps be the most convenient term to apply to the cause of the increased period of oscillation which such association entails; but, of course, any systematic obstruction to vibration, any drag, would have the same effect as the drag of inertia.

§ 190. In some experiments relating to the "wandering of the ions" in jellies during electrolysis, which I had the honour of bringing before the Physical Society on the 16th of March, 1878, I described the spreading of the acid and alkaline ions through the unmelted jelly. These results I do not publish, because a friend has had the great kindness to point out to me that many of the results which were then exhibited had been obtained several years previously by Dr. W. M. Ord. The experiments and speculations of Dr. Ord are contained in a very remarkable and suggestive series of papers contributed chiefly to the St. Thomas's Hospital Reports *. Amongst the jellies which I then prepared but did not exhibit, was a stiff gelatine jelly saturated with sulphate of copper. This jelly was of a bright emerald-green by transmitted light. On exposure to the air of a portion which had not been subjected to electrolysis, the water gradually evaporated and the salt began to crystallize out. The form of the crystalline masses was curiously modified by the jelly. Rounded masses were formed, reminding one of my friends of the coccoliths of the deep-sea dredgings—another, of the mineral or uric concretions

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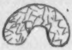
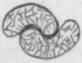
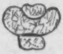
* "Some Experiments relating to Forms assumed by Uric Acid" (St. Thomas's Hospital Reports, 1870); "An account of some Experiments relating to the Influence exercised by Colloids upon the Forms of Inorganic Matter" (St. Thomas's Hospital Reports, 1871); "Studies in the Natural History of the Urates" (Rep. Microscopical Society, Jan 6, 1875); "On some Points in the Natural History of Uric Acid and Urates" (St. Thomas's Hospital Reports, 1875); "Urinary Crystals and Calculi," &c. (Medico-Chirurgical Transactions, vol. lviii. March 9, 1875).

which occur in mucous media—and yet another, of "chlorite." Whether there be, as is most likely, a common cause, a colloid medium, in all the three cases, I must not here discuss. The ultimate crystalline element is too minute for determination; but the elements of secondary form invariably resemble (1). These elements are frequently linked two by two in one plane (2), or at right angles to one another (3). The convex sides are generally very deeply furrowed, so as to give the impression of their being four secondray elements. These concretions can be picked out of the jelly in which they form, like almonds out of a cake. So clean is their separation, and so feeble their blackening when heated with oil of vitriol, that they must be regarded as homogeneous bodies free from gelatine; and their composition is therefore of no common interest. Ten of these concretions, which are remarkably uniform in size, weighed 0·5024 gram; the loss on heating to 200° C. in an air-current was 0·1432 gram, showing 28·504 per cent. of water. This points to the formula $CuSO_4 + 3{\cdot}5\,H_2O$; and, as I hope to show in my next communication, the subdivision of the water molecule in hydrated sulphate of copper, or rather the multiplication of the whole formula of that salt, does not admit of doubt. Here again we have evidence of the continuity of composition according to physical circumstances (compare § 142). But what a complete chain of difference of diffusive potential is here indicated, stretching from the first nucleus throughout the jelly! and how it suggests the diffusion and accretion of the matter of a crystalline mineral through a colloid and, perhaps, mechanically rigid mineral matrix!


(1)


(2)


(3)

To return to the green colour of the copper jelly. Gelatine is so complex a body, that although the formation of the blue crystals of the sulphate shows that there has been no general chemical change, yet there is no evidence of its entire absence. Glycerine was therefore next employed as a medium for the solution of various coloured salts.

§ 191. Anhydrous sulphate of copper dissolves so abundantly in glycerine that the solution may be almost solid when cold. There is no sign of crystallization; but the solution at all strengths is a bright emerald-green.

§ 192. Crystals of permanganate of potassium, when heated with glycerine, oxidize it with the escape of gas; but if cold glycerine is added to a cold saturated aqueous solution of the permanganate, a liquid is obtained, without evidence of chemical change, which has been pronounced to be brownish yellow, amber, or, perhaps more accurately, "raw-sienna." In view of the possible chemical change which may be incipient here, it is perhaps better to put this result on one side.

§ 193. Chloride of cobalt, which in water gives the well-known pink hues according to its strength, gives with glycerine a beautiful carmine; this, when heated, is greatly enriched in its blue. When cooled in a carbonic acid cryogen, it acquires a yellowish tint.

§ 194. Chromium potash alum, which in water gives the pale indigo of dilute ink, gives with glycerine an emerald-green.

Whatever be the degree of intimacy of association between the glycerine and the salt, it appears, then, that this association does in all cases retard the light-wave period, or increases its length. The bluing of the cobalt-glycerine solution by heat, and its yellowing by cold also, are entirely in accord with the before-mentioned conception. It may be noticed also that the glycerine solution of a coloured salt is, as a rule, of a much richer colour than the aqueous solution of the same strength by weight or volume.

I cannot but think that these results lend considerable support to the idea mentioned in § 189, which idea has been so far fruitful in Abney's hands that he has been enabled, by associating a metallic salt with a heavy molecule, to fit the vibrating period of a photographically sensitive film to the light which it is desired to record.

I have to express my indebtedness to Mr. A. K. Huntington for the patience, zeal, and skill which he has shown in helping me in the work of the first half of this part (No. VI.) of my research.

XXX *On the Transmission of Vocal and other Sounds by Wires.* *By* W. J. Millar, *C.E., Sec. Inst. Engineers and Shipbuilders in Scotland.*

1. *Object of Paper.*—The object of the present paper is the description of a series of experiments made by the author upon the transmission of vocal and other sounds by wires, and the results obtained from those experiments.

2. *Transmission of Sound in general.*—The transmission of sound by various media is familiarly illustrated from day to day; and the readiness with which these media are affected has been made the subject of many experiments.

One familiar illustration of the transmission of sound from air to solids and thence back to the air is that which occurs in the vertical and horizontal partitions between rooms, such as partition walls and floor and ceiling spaces—the sounds originating in one room being thus transmitted to the adjoining room without having recourse directly to air communication.

From a consideration of the latter, as also from other phenomena, the author has for some time been convinced that vocal sounds might be transmitted by solid bodies, such as wires, and that to considerable distances.

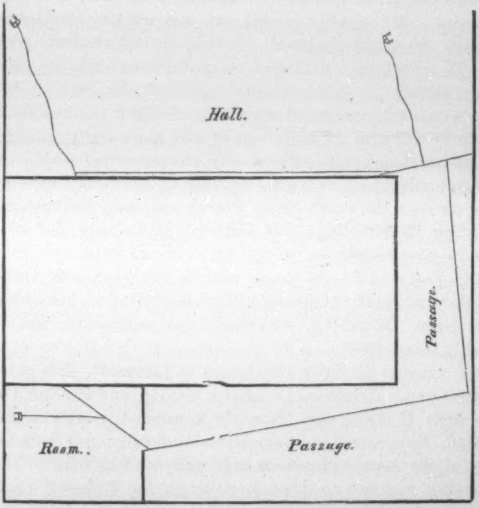
After several unsuccessful atttempts, the author during the month of January last, having occasion to use some fine copper wire, carried a portion of it out from the house to a distance of about 20 yards, and attached a couple of pasteboard disks with low rims to the ends of the wire: the transmission of vocal sounds was then found to be easily effected, conversation being readily carried on through this length of wire.

Since that time the author has made many experiments with various combinations and under various circumstances. The principle upon which they all more or less appear to depend, so far as the rendering audible of the sounds, is that of the tuning-fork and sounding-box, in which the sound from the vibratory movements of a metal body is considerably intensified when the body is placed upon a sonorous substance affecting the air in its vicinity.

3. *Notes of some of the more important Experiments.*

(1) No. 23 copper wire was stretched between windows outside of house, and attachments at right angles made to rooms through the windows. Speaking in one room was then heard in the other; the distance was about 20 yards. Pianoforte music was easily transmitted by placing an ear-piece inside the instrument and carrying the other end of the wire outside the house.

(2) No. 40 copper wire fitted up in a building, passing from room to room as per diagram below. Six attachments and angles.



Distance about 50 yards. Conversation, singing, whistling, breathing, and the sound of a light C tuning-fork ($2\frac{1}{4}$ inches in fork) readily transmitted.

Various similar arrangements were also made in house from room to room, and finally carried to a distance outside, when all the above effects, as also the transmission of whispering, were clearly demonstrated, the persons at either end being quite out of hearing in the ordinary manner.

The communication was not limited to the persons at either end of the wire; additional connexions were occasionally made, when three or more individuals could communicate with each other.

(3) Carried about 7 yards of No. 23 copper wire from one room through an adjoining one to a room beyond, the wire in its course passing *below two doors* shut above it, and for the most part in *contact with the carpet*, but fastened at the ends so as to produce some tension. Made two connexions of No. 40 copper wire at angles with the main wire; conversation was then readily carried on, and all the phenomena already described produced. Subsequent experiments with No. 16 copper wire arranged as above were found to yield better results.

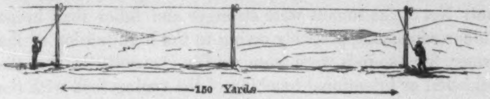
A somewhat similar and equally successful experiment was made by carrying the same size of wire down stairs, passing below two doors and partly resting on carpet and wood. A positive advantage is gained by resting the heavy wire in this manner, the words being clearer and more distinct, and free from the rumbling sound occurring with a suspended wire free to move about.

(4) Fastened No. 23 copper wire to telegraph-wire, made another and similar attachment 75 yards further on, but within two posts. Breathing, whistling, and tuning-fork sounds readily transmitted.

(5) Carried the latter attachment to 150 yards, thus *passing one post*. Breathing, whistling, singing, and the sound of the light C tuning-fork, formerly mentioned, readily transmitted. No apparent loss though passing the support (the latter was of the usual china-ware cup with binding-wire). The speaking was not so distinct, although the different word-sounds were discernible. This can be accounted for by the fact that, as the poles were about 14 feet high, the attachment-ends were free to swing about, which, combined with the exposed situation of the main line, gave rise to a considerable vibratory action due to other causes than the vocal sounds. (See diagram, page 293.)

(6) About 50 yards of No. 23 copper wire was laid out so

as to rest partly on grass, and fastened up at the ends to pins; attachments were made, and vocal sounds transmitted: whistling and the tuning-fork sounds very clearly heard, although a high wind was blowing at the time.



4. *The Mouth- and Ear-pieces.*—The mouth- and ear-pieces used in these experiments have been of various materials and forms. The materials tried have been pasteboard, wood, gutta-percha, india-rubber, parchment, iron, tin, and zinc. These have generally been arranged as disks or drums, having a more or less extended rim around them to confine the sounds. This rim has been of cylindrical, conical, and other forms.

In general, greater volume of sound accompanied increased depth of rim; but the sounds were hardly so distinct as when the rim was kept shallower.

The wire was usually attached to centre of disk; but in some cases good results were got where the wire was led through a cylindrical hollow piece of wood and terminated *close* to the disk; indeed a hollow piece of wood *without* a disk did very well.

As a rule, the effects seemed better when the wire was led outside of the house.

High-pitched voices are more easily heard than deep strong voices.

In the experiments with the telegraph-wire one of the disks used was of thin sheet-iron 3½ inches in diameter. Set in a wooden rim about ½ inch deep, the wire was fastened into a small piece of wood, which in turn was cemented down to centre of disk. The tuning-fork sounds were very well heard with this arrangement; and one peculiarity was that, on the wooden fastening accidentally breaking away from the iron, the sounds could again be heard by holding the disk in one hand and pressing the wooden termination of the wire upon the disk with the other.

5. *Wires.*—The wires, as a rule, require to be more or less tightened up; but this varies with the heaviness of the wire.

The sound is increased with a tight wire.

The volume of sound appears to be increased with a heavy wire. Thus in the telegraph-wire about $\frac{1}{8}$ inch thick, probably No. 8, the sounds were stronger and fuller than in the thinner wires, and, probably owing to the high tension of the former, faint sounds were more readily transmitted: thus the accidental or intentional touching of the tuning-fork with the rim of the mouth-piece, causing a slight clicking sound, was distinctly heard through the ear-piece at a distance of 150 yards—and this, even although the two attachments of copper wire were practically at right angles to the main wire, whereby part of the sound would pass away onwards up and down the line.

6. The great delicacy of the action may be inferred from the fact that fine sand strewn upon the disk of the ear-piece is unaffected by conversation through lengths of about 7 yards. The sensitiveness also of the mouth-piece was shown by sounds *not spoken into it* being readily transmitted, such as coughing, laughing, or remarks made by persons standing beside the instrument. Indeed, in some cases an advantage is obtained by keeping back from the mouth- or ear-pieces; and the author has sometimes thought an improvement was obtained by holding the ear-piece slightly inclined to the ear.

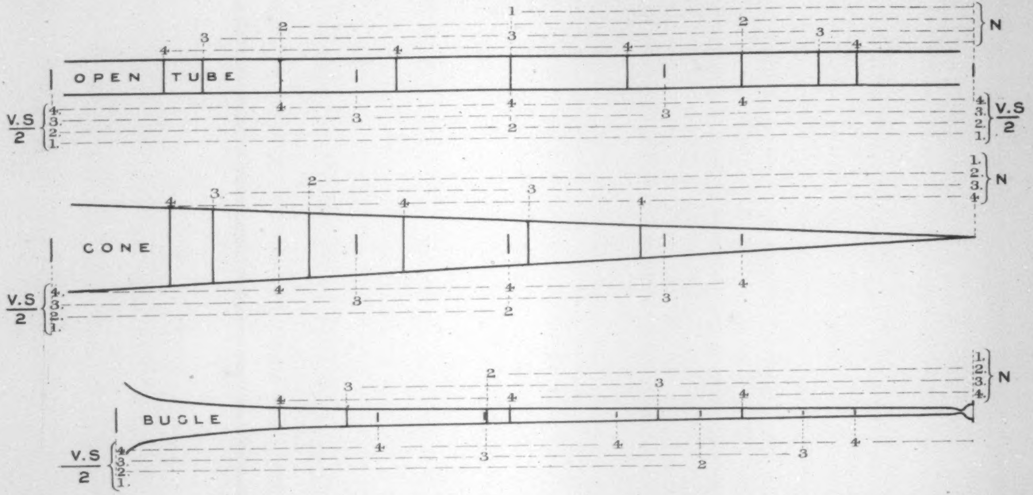
In all cases the individual voice could easily be distinguished though modified more or less by the structure and material of the mouth- and ear-pieces.

The mouth- and ear-pieces were usually of the same form and material, and were therefore used for either speaking or hearing. Some forms, however, do better as ear-pieces, others as mouth-pieces.

In conclusion, the author believes that many interesting physical questions may be studied by means of these arrangements, and that practical application may be made where communication of this nature is required.

NODAL POINTS.

Scale – ⅛ full size.


OPEN TUBE
CONE
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D.J.B. del.
Mintern Bros lith.

XXXI. *The Electrical Properties of Bees'-wax and Lead Chloride. By* W. E. Ayrton, *Professor in the Imperial College of Engineering, Tokio, Japan.*

[Plate VII.]

In the two papers by Prof. Perry and myself on Ice as an Electrolyte, recently read before the Physical Society, we showed that both the conductivity and specific inductive capacity of $\left\{\begin{matrix}\text{ice}\\ \text{water}\end{matrix}\right\}$ increased regularly, without discontinuity, in passing from several degrees below the freezing point to several degrees above it. We drew attention to the fact that, in consequence of the absorbed charge in water being immeasurably greater than the surface-charge, we could not hope, by any method of experimenting, to properly compare the true specific inductive capacity with the index of refraction for light of infinitely long waves; so that, in fact, the only support that Prof. C. Maxwell's electromagnetic theory of light could hope to derive from these experiments must be based simply on the fact that in $\left\{\begin{matrix}\text{ice}\\ \text{water}\end{matrix}\right\}$ both the specific inductive capacity and the index of refraction increase as the temperature rises. At the meeting of the Society on November 3rd, at which the second of our two papers was read, Prof. G. Foster mentioned that he had recently been collecting all the results he could find connecting specific inductive capacity with index of refraction. I therefore beg to forward, as a contribution to this collection, the following results of some further experiments which I have been making on this subject.

For the last two years my attention has been turned to wax as a good material for electrically testing, especially in regard to the connexion which, in our paper on the Viscosity of Dielectrics, communicated to the Royal Society, we pointed out existed between high specific inductive capacity and low specific resistance. I therefore had constructed a large condenser, consisting of many sheets of letter-paper soaked in melted bees'-wax, with alternate sheets of tin-foil. After the condenser was built up in the usual way, melted bees'-wax was poured in, the plates squeezed together, and the whole shut up in a fairly good water-tight wooden box. The condenser was buried several feet under ground, to ensure uniformity of temperature, connexion being made with the insulated coating by a piece of Atlantic-cable core, and with the other coating by a piece of bare copper wire.

After this condenser had been buried for a short time underground, it showed the apparently abnormal condition of diminution of resistance by electrification. This phenomenon then formed the subject for special investigation with this condenser, an account of the results obtained being given at the end of this short paper.

As bees'-wax is one of the few substances in which the index of refraction for light increases in passing from the liquid to the solid state, it seemed important, in connexion with the electromagnetic theory of light, to carefully measure the specific inductive capacity of a wax condenser as it was gradually cooled through the solidifying point. A small, shallow, clean copper box, 19 centims. long by 17 centims. wide, was therefore lined with a sheet of letter-paper, 0·036 centim. thick, previously well soaked in melted bees'-wax. A clean copper disk, 12·8 centims. in diameter, was placed on the top, weighted down, and the dish filled up with melted wax. This condenser, A B (fig. 1), was heated in an oil-bath, C D. E and F are holes for the insertion of thermometers, of which the bulbs were just above the wax condenser; G is an opening through which the insulated electrode H of the condenser may protrude without touching the oil-bath. A wooden stand, W W, supports the condenser in the middle of the bath; and a glass vessel V holds strong sulphuric acid to keep the inside space artificially dry. The bath is closed by a double door, which is made to fit well by a strip of leather inserted between it and the bath.

The condenser having been inserted, the bath was heated to about 90° C., and kept at that temperature for some time; the lamps were then removed, when the temperature fell very slowly. The capacity was then measured (several observations being made at each temperature) by charging the condenser with 75 Daniell's cells joined in series, and discharging it through an exceedingly delicate Thomson's reflecting galvanometer. The curves A B C D, E F G, H J K (fig. 2) represent the results obtained on three different days, distances measured parallel to O X representing temperature, the points O and X corresponding respectively with 0° C. and 100° C., and distances measured parallel to O Y representing capacity, the zero-line for capacity for the curves A B C D, E F G, being below O X by a distance equal to $\frac{2}{3}$ of O Y. For the curve H J K the zero-line is O X. It will be seen at once that these curves, obtained on different days, do not give the same capacity for the same temperature (the numbers, therefore, that have been calculated for the specific inductive capacity are not given); but considering, first, the very small capacities that had to be measured, and, secondly, the difficulty of accurately determining the temperature of a non-heat-conductor like wax, even when enclosed in the oil-bath, the discrepancies in the curves are not to be wondered at. One fact, however, is very striking in all the three curves; and that is the *rise* in capacity as the temperature very slowly falls from about 80° to 60° C., and the subsequent diminution in the capacity on a still further diminution of the temperature. Probably, had experiments on capacity been made when cooling from a much higher temperature, there would have been observed, first, a gradual diminution in capacity due to cooling down to about 80° C. (traces of this first diminution are seen in the portion A B of the curve A B C D); then we have the rise of capacity as the wax solidifies at about 60° C.; and, lastly, we see the subsequent rapid decrease on further cooling. Now this is precisely in agreement with the changes known to occur in the index of refraction for light; and hence the interest of these experiments.

As there was always a small electromotive force in the wax condenser, and as the vibrations of the galvanometer-needle were, as usual, damped by the air-vane, I used for calculating the capacity the formula developed by Prof. Perry and myself for employment in such cases*, which is

$$Q=\frac{H}{lG}\frac{P}{2\sqrt{\pi^2+L^2}}\left[\left\{(x_1-x_r)^2\epsilon^{2\frac{L}{\pi}\tan^{-1}\frac{\pi}{L}}-\frac{\pi^2}{\pi^2+L^2}x_r^2\right\}^{\frac{1}{2}}+\frac{L}{\sqrt{\pi^2+L^2}}x_r\right],$$

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* 'A Test for determining the Position of a partial Discontinuity, without Earth-fault,' by Professors W. E. Ayrton and John Perry, p. 12.

where Q is the quantity of electricity discharged through the galvanometer, H the horizontal intensity of the galvanometer-field, l the half length of the needle, G the galvanometer-constant, P the periodic time of vibration, L the logarithmic decrement, x_1 the first sudden swing on discharge, x_r the deflection that would be produced by the small constant current, and which is equal to

$$\frac{x_1 + Dx_2}{1 + D},$$

where x_2 is the second swing and D the decrement.

It might, of course, be at once objected that the rise in capacity as the wax cools from about 80° to 60° C. is perhaps not due to any change in the specific inductive capacity, but merely indicates that the distance between the copper plates of the condenser was slightly diminished by the wax shrinking on solidifying. This solution, however, is improbable, since, although a sudden expansion of the wax on solidifying (if such an expansion existed) might have separated the plates, it is unlikely that the contraction which really occurred could have brought them nearer together than the thickness of the paper by which they were separated when the wax was liquid. Nevertheless, partly to obtain additional evidence on this point, and partly to measure the specific resistance (or resistance per cubic centimetre) of bees'-wax at different temperatures, I made ten distinct sets of experiments, occupying many days, on the conductivity of wax. In these experiments the wax condenser was heated up to about 130° C., and a current sent through it with the 75 Daniell's cells in series. The temperature was kept constant at about 130° C. until the galvanometer-deflection had reached its maximum, when it was considered that the wax had acquired the temperature indicated by the thermometer. The temperature was then allowed to fall very slowly, and frequent readings of the galvanometer and thermometer were taken. The results obtained are shown on fig. 3, temperature being measured parallel to O X, the points O and X corresponding with 30° and 130° C.; distances measured parallel to O Y represent conductivity on such a scale that for the curve L M, representing the conductivity between 115° and

65° C., O S corresponds with a resistance of 67,735 megohms per cubic centimetre; and for the curves N P, Q R (which are drawn on a larger scale) the distance O T represents a resistance of 186,000 megohms,—the zero-line for conductivity for all three curves being O X. The point P, corresponding to a resistance of 37,000,000 megohms per cubic centimetre, represents the lowest conductivity I was able to measure with certainty directly with the galvanometer. It may here be mentioned that such high resistances could be measured with the galvanometer, since one Daniell's cell, through a resistance of 600 megohms, gave 130 scale-divisions deflection on a scale about 1½ metre distant. The various curves obtained for conductivity between 115° and 65° C. agree so closely that they may all be represented by the one curve L M. The curves for the conductivity between 80° and 40° C. are all quite regular, but not all of exactly the same slope, the difference depending on the highest temperature to which the wax was heated before cooling on the particular day of experimenting, this being sometimes about 130° C. and at other times about 90° C. All the curves, however, agree so closely that they are all contained between the two limiting curves N P and Q R shown in fig. 3. In no curve was there *the slightest appearance* of a rise of conductivity at the melting-point, which would probably have been obtained had the copper plates approached one another an appreciable distance on the wax solidifying.

We may therefore conclude that in the previous experiments the rise in the capacity in solidifying indicates a true increase in the specific inductive capacity coincident with an increase in the index of refraction for light.

As regards apparent increase of resistance by electrification, which, as mentioned, I observed during repeated experiments, extending over some months, with the wax condenser buried underground, the general conclusions arrived at were that not only did the conductivity usually increase by electrification, but that it steadily increased day by day—a result indicating that the wax was deteriorating, probably from damp penetrating through the joints of the wooden box in spite of leather having been inserted between the different parts of the wood before they were screwed together. This conclusion appeared to be correct, since, on digging up the condenser and keeping it near a fire for many days, it regained its original high resistance. The damp must therefore not only have entered through the joints in the wood, but through some small cracks that were observed in the mass of wax when the condenser was opened ; and it was probably due to this damp that the peculiar effects of polarization were observed similar to those noticed by the Comte du Moncel when testing stones, and by Mr. T. Warren in certain insulating oils.

I now made a number of experiments with lead chloride as a dielectric—a substance to which my attention was especially drawn by some remarks of M. Buff in *Ann. Chem. Pharm.* cx. p. 258 (1859), in which he says that this substance conducts electricity like a metal (that is, without decomposition)—a conclusion, however, which at first sight would appear to be negatived by certain experiments of M. Wiedemann published in *Pogg. Ann.* cliv. 318–320, from which he found that the resistance of lead chloride diminished by increase of temperature.

I first had made a small carbon box containing a carbon plate, but prevented from touching it by three small pieces of clean glass. The carbon plate had a carbon electrode attached to it, the whole being cut out of a solid piece of carbon so as to have the shape of an inverted T. Into the box lead chloride was poured in a fused state until it covered up the plate, but leaving the carbon electrode of the plate protruding for connexion with the battery. The whole was then allowed to cool very slowly. The outer part of the carbon box and the end of the carbon electrode were now electrotyped, and copper wires soldered on, the junctions of the carbon and copper being quite clear of the lead chloride.

With this condenser the results given on the next page were observed.

In addition to the resistance of the condenser being measured while the battery was connected, time-readings were also taken with the galvanometer of the discharge from the condenser after the removal of the battery, as well as time-readings with an electrometer of the electromotive force in the condenser producing the discharge. As, however, the diminution in the discharge-deflection was in each case quite regular, the curves are not given.

No. of exp.	Date.	Temp.	Battery.	Resistance of the wax condenser, in megohms,				Remarks.
				after 15 sec.	after 30 sec.	after 1 min.	After	
1.	Nov. 13th ...	18°·8 C.	31 volts copper pole to carbon box......	7·97	8·077	7·875	14 min., 6·774	Steady diminution in resistance from the middle of the first minute.
2.	Nov. 13th ...	18°·8 C.		......	7·848	8·158	14 min., 6·326	Steady diminution in resistance from the end of the third minute.
3.	Nov. 14th ...	19°·9 C.		......	10·15	9·706	5 min., 8·682	Steady diminution in resistance from the first observation.
4.	Nov. 15th ...	18°·5 C.		9·254	9·118	9·323	8 min., 7·607	Steady diminution in resistance from the end of the first minute.
5.	Nov. 21st	....	30 volts copper pole to carbon box......	5·477	5·128	5·128	14 min., 3·951	Steady diminution in resistance from the beginning.
6.	Nov. 24th ...	....	30 volts copper pole to carbon plate ...	4·874	5·770	......	12 min., 4·365	Steady diminution in resistance from the middle of the second minute.
7.	Nov. 26th ...	....	30 volts copper pole to carbon box......	5·755	6·167	6·167	8 min., 5·820	Steady diminution in resistance from the beginning of the second minute.
8.	Nov. 27th ...	....		5·911	6·186	5·911	9 min., 4·708	Steady diminution in resistance from the middle of the first minute.
9.	Nov. 28th ...	....		6·174	6·174	6·174	6 min., 5·409	Steady diminution in resistance from the beginning of the second minute.
10.	Nov. 29th ...	....		......	......	6·476	6 min., 5·440	Steady diminution in resistance from the beginning of the second minute.
11.	Nov. 30th ...	....		7·875	8·100	7·875	10 min., 6·163	Steady diminution in resistance from the middle of the first minute.
12.	Dec. 1st......	....		8·621	8·493	8·129	5 min., 7·295	Steady diminution in resistance from the commencement.

Condenser well discharged between every two tests.

It is interesting to observe in the Table (p. 303) that in *every* case there is a diminution of resistance by electrification, although in some cases there was an increase during the first minute. Looking at the first group of tests, taken between November 13th and 15th, we see a gradual increase in the resistance day by day. Looking also at the second group made between November 21st and December 1st, we likewise see a steady daily increase in the resistance; but in the interval between November 15th and 21st, when no tests were made, there appears to be a decided diminution in resistance. Considering, however, that the tests taken on November 13th, at the beginning, and on December 1st, at the end of the investigation, give almost identical results, it cannot be concluded with certainty that there was any decided deterioration taking place in the lead chloride. But on breaking up the condenser, the lead chloride was found to contain many small holes; so that it is possible that damp may have collected in these. This solution, however, would at first sight appear to be rather improbable; since the condenser, both when being tested and when not tested, remained in an atmosphere kept partially dry with sulphuric acid.

Some fresh lead chloride was prepared in the same way as before—that is, by precipitating from a solution of lead acetate with a solution of common salt, and carefully washing the precipitate several times with distilled water. But the new condenser, made with the carbon box and plate, was found to have a resistance of only two megohms at 16° C.; and, unlike what was experienced in the former case, the resistance in all the experiments was now found to increase by electrification. This, however, is probably explained by the fact that, whereas in the previous case thirty volts electromotive force was used, now only one volt was employed; so that decomposition (whether of the lead chloride itself, or of the damp which after decomposition may act on the chloride) was probably not produced. Some preliminary temperature-tests were now made; and, in accordance with Wiedemann's results, I found that the resistance diminished with elevation of temperature.

The condenser was now left in an atmosphere dried with sulphuric acid from December 21st to January 7th, when it was found that the resistance had increased to about 15·6 megohms at 70° C. A large number of measurements of the conductivity at different temperatures, using the same oil-bath for raising the temperature as is shown in fig. 1, were now made. The different experiments gave results so nearly agreeing that they may all be represented by the curve S T V (fig. 4), in which distances parallel to O X represent temperature, the points O and X corresponding to the temperatures 0° and 100° C. respectively; and distances parallel to O Y represent conductivity on such a scale that the point T, corresponding to a temperature of 70° C., represents a resistance of about 15·6 megohms. The curve is approximately logarithmic; that is, the ratio of the difference of the logarithms of the conductivities to the difference of temperatures is approximately constant.

Thinking that possibly the method previously employed for making the lead chloride, by precipitating it from a solution of lead acetate with a solution of common salt, may have introduced traces of some salt of lead other than the chloride, the following method was now employed for making another supply of the chloride. From a clear solution of lead nitrate a precipitate was formed with colourless hydrochloric acid, and the precipitate well washed with distilled water. A third condenser was now constructed, three small pieces of glass 0·225 centimetre thick being used to separate the carbon plate from the box. The connexions with the box and plate were made as before, by first electrotyping the carbon with copper and then soldering on copper wires, the junctions of the carbon and copper not being in contact with the lead chloride. A condenser was also made with a copper box and a copper plate, the two being well coated with graphite to protect them from the action of the lead chloride, and separated from one another by three small pieces of glass 0·135 centimetre in thickness.

Tests of conductivity were now made at different temperatures with both condensers, 0·075 volt being employed with the carbon and 7·5 volts with the copper condenser, or sometimes 2·2 volts with the latter. With the carbon condenser and with the smaller electromotive force the resistance was found to increase with electrification, whereas with the copper condenser and with the electromotive force 2·2 volts the resistance diminished with electrification, and with 7·5 volts this diminution became much more rapid, these results being observed at both high and low temperatures. In the earlier experiments with this copper condenser the diminution was regular, whereas later on it proceeded irregularly; but on the whole it may be said that when an electromotive force not exceeding 1¾ volt was employed there was an increase in resistance by electrification, such as is usually experienced with gutta-percha and with ordinary dielectrics, while when the electromotive force exceeded this limit there was either a regular or an irregular diminution of resistance by electrification—the results apparently not depending much on whether carbon or copper coated with graphite was used for the plates of the condenser.

As this limiting electromotive force appears to be about the same as that necessary to decompose water, I think we may fairly conclude that the diminution in resistance is due to a decomposition of the damp (which appears to be contained in the lead chloride even when careful means are taken to dry it), and to the products of the decomposition acting on the chloride. Fig. 5 shows four electrification-curves, A A A, B B B, C C C, D D D, obtained from four *successive* experiments with the carbon box, and corresponding with the temperatures 15° C., 57° C., 14° C., 61° C. respectively. Time is measured parallel to O X, the points O and X corresponding to the moment of applying the battery, and to 50 minutes afte wards; conductivity is measured parallel to O Y from the line O X of zero conductivity. The curves B B B and D D D, for 57° C. and 61° C., are drawn on a vertical scale five times smaller than that employed for A A A and C C C—the scale for time, however, remaining the same. All the tests from which these curves are drawn were made with 0·075 volt electromotive force. The curves *a a a*, *b b b*, *c c c*, fig. 6, are the discharge-curves obtained in the three above experiments for 15° C., 57° C., and 14° C., observations of the discharge in the experiment for 61° C. not having been taken. The scale both for conductivity and for time is the same exactly as that employed in the curves A A A, C C C, fig. 5. All the curves show a regular increase of resistance with electrification, the increase being far more rapid at a high than at a low temperature. As was seen from the curve S T U, fig. 4, so also from fig. 6 we learn that the conductivity is much greater at a high than at a low temperature; and we also see from the curves A A A, B B B, C C C, D D D that the general effect of testing day by day appears to lower the conductivity.

Electrification-curves E E E, F F F, G G G, H H H, fig. 7, were obtained from four *successive* tests with the copper-box condenser, and correspond with the temperatures 15° C., 60° C., 13° C., 61° C. respectively. Time is measured parallel to O X, the points O and X corresponding to the moment of applying the battery; and 50 minutes afterwards conductivity is measured parallel to O Y from a zero as far below O X as the point Y is above. Curve F F F is on a scale for vertical distances one twentieth of that employed for the curves E E E G G G, and H H H on a scale one fifth of that used with E E E, G G G: that is to say, if the same scale were employed for vertical distances for all four curves, the two for the higher temperatures would be far above those for the lower temperatures—in fact, would be off the paper altogether. For horizontal distances (that is, for time) the same scale is employed for all the curves. An electromotive force of 7·5 volts was employed with all the experiments from which these four curves were drawn. Although the curves are irregular, still, on the whole, there is an increase of conductivity or diminution of resistance with electrification; and that this is probably due to the chemical action of the current referred to above is shown from the irregularity of the discharge-curve *g g g* obtained after removing the battery in the test at 15° C. Curve *h h h*, however, which is the discharge-curve for the test at 61° C., does not show any such irregularity; but then it must be noticed that H H H, the charge-curve for this temperature, indicates on the whole rather an increase than a diminution of resistance by electrification.

I have to thank three of my students, Messrs. Asano, Fujioka, and Nakano, for valuable assistance rendered during the course of this investigation.

April 1st, 1878.

XXXII. *Recent Researches in Solar Chemistry.*

By J. N. Lockyer, *F.R.S.*[*]

The work which is now being done in the various new fields opened up in connexion with solar studies may be conveniently divided into three perfectly distinct branches. We have, first, that extremely important branch which has for its result the complete determination of the position of every thing which happens on the Sun. This, of course, includes a complete cataloguing of the spots on the sun which have been observed time out of mind, and also of those solar prominences the means of observing which have not been so long within our reach. It is of the highest importance that these data should be accumulated, more especially because it has been determined that both in the case of spots and prominences there are distinct cycles, which may in the future be very much fuller of meaning to us than they seem to be at present.

This brings me to refer to the second branch of the work; and it is this:—These various cycles of the spots and prominences have long occupied the attention both of meteorologists and magneticians; and one of the most interesting fields of modern inquiry, a field in which very considerable activity has been displayed in the last few years, is one which seeks to connect these various indications of changes in the sun with changes in our own atmosphere. The sun, of course, is the only variable that we have. Taking the old view of the elements, we have fire represented by our sun, variable if our sun is variable. Earth, air, and water, in this planet of ours we must recognize as constants. From this point of view, therefore, it is not at all to be wondered at that both magneticians and meteorologists should have already traced home to solar changes a great many of the changes with which we are more familiar. This second branch of work depends obviously upon the work done in the first, which has to do with the number (the increasing or decreasing number) of the spots and prominences, and the variations of the positions which these phenomena occupy on the surface of the sun. As a result of this work, then, we shall have a complete cataloguing of every thing on the sun, and a complete comparison of every thing on the sun with every meteorological phenomenon which is changeable in our planet.

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[*] Read May 11, 1878.

When we come to the third branch of the work, the newest branch, things are not in such a good condition. The workers are too few ; and one of the objects of any one who is interested in this kind of knowledge at the present moment must be to see if he cannot induce other workers to come into the field. The attempt to investigate the chemistry of the sun, even independently of the physical problems which are, and indeed must be, connected with chemical questions, is an attemps almost to do the impossible unless a very considerable amount of time and a very considerable number of men be engaged upon the work. If we can get as many workers taking up various questions dealing with the chemistry of the sun as we find already in other branches, I think we may be certain that the future advance of our knowledge of the sun will be associated with a future advance of very many problems which at the present moment seem absolutely disconnected from it.

I have today to limit myself to this chemical branch of the inquiry ; and first let me begin by referring to the characteristics of the more recent work with which I have to deal. Here, as in other branches of physical and chemical inquiry, advance depends largely upon the improved methods which all branches of the science are now placing at the disposal of all others. Our knowledge of the chemical nature of the sun is now being as much advanced by photography, for instance, as that descriptive work of which I spoke in the first instance (which deals with the chronicling and location of the various phenomena) has, in its turn, been advanced by the aid of photography. I do not know whether the magnificent results recently obtained by Dr. Janssen have been brought before this Society ; but the increase in photographic power recently secured by Dr. Janssen is one which was absolutely undreamt of only a few years ago. It is now possible to record every change which goes on on the sun down to a region so small that one hardly likes to challenge belief by mentioning it. Changes over regions embracing under one second of angular magnitude in the centre of the sun's disk can now be faithfully recorded and watched from hour to hour.

One of the advantages which has come from the introduction of the new apparatus has been the possibility of making maps, on a very large scale, of the solar lines and of the metallic lines which have to be compared with them. Thanks to the great generosity of Mr. Rutherfurd, who is making the most magnificent refraction-gratings which have ever been seen, and who is spreading them broadcast among all workers in science, one has now easy means of obtaining with inexpensive apparatus a spectrum of the sun, and of mapping it on such a scale that the full magnification of the fine line of light which is allowed to come through the slit will form a spectrum the half of a furlong long: an entire spectrum on this scale, when complete (as I hope it some day will be, though certainly not in our time) from the ultra-violet, already mapped by Mascart and Cornu, to the ultra-red, which has quite recently for the first time been brought under our ken by Captain Abney, will be 315 feet long. This is a considerable scale to apply to the investigation of these problems; but recent work has shown that, gigantic as the scale is, it is really not beyond what is required for honest patient work. I have already had an opportunity of bringing before the Physical Society several of the methods in use for comparing the spectra of the various elementary bodies with that of the sun. It is not, therefore, necessary now to refer to them. There are, however, others of recent application which are of very considerable importance.

When, instead of inquiring into the coincidence of the metallic lines, we wish to determine the coincidence of the lines due to various gases, the method hitherto employed has been to enclose the gases in Geissler tubes, to reduce their pressure, and in that way to fine down the lines. The importance of this apparently small matter can be very well demonstrated by an experiment easily arranged in an electric lamp, which sodium enables us to perform without any great difficulty. The point of this experiment is that, if we vary the density of any vapour, we vary sometimes to a very considerable extent the thickness and intensity of the lines. I am about to throw the spectrum on a small screen which I have behind the lamp; and I hope I shall succeed in rendering the phenomena visible. I want you to observe the variation in the thickness of the reversed line of sodium. Every turn of the screw which raises or lowers the upper pole, enables me to vary to a very considerable extent indeed the thickness of that absorption-line.

Now the way in which that has been managed is very simple. The only arrangement required is one which shall enable me at will to vary the density of the sodium-vapour. When I make the sodium-vapour as dense as possible, then the line is very thick. When I make it much less dense, the line becomes thinner. If the spectrum on the screen had been a gas-spectrum (supposing it were possible to exhibit a gas-spectrum to an audience), the exact equivalent of that experiment would have been, that the gaseous spectrum at atmosphere pressure would have given us most of the lines as thick as the sodium-line was at its thickest; while if by any possibility we could have rendered the phenomena visible while the pressure was being reduced, as the pressure of the gas was reduced the line would thin. Now there are very great objections to the using of Geissler tubes. One very valid objection is that the gas becomes much less luminous as its pressure is reduced.

Here is a method which is excellent in this way, that it enables all the work connected with gaseous spectra to be done at atmospheric pressure, and we get the line down as thin as we choose, *not by reducing the pressure*, but by *reducing the quantity of gas in a mixture.* If we take, for instance, a spark in ordinary atmospheric air and observe its spectrum, we find the lines of the constituents of atmospheric air considerably thick; but if I wish to reduce the lines, say of oxygen, down to a considerable fineness so that I can photograph its lines (these should be fine, in order to enable me to determine their absolute position; to accomplish this) the spark is made to pass in a glass vessel with two adits and one exit tube. If I wish to observe the oxygen-lines fine, I flood the vessel with nitrogen so that, say, there is only 1 per cent. of oxygen present, and observe the current between the enclosed electrodes. If I wish to observe nitrogen-lines fine, I flood it with oxygen, so that there is only 1 per cent. of nitrogen present. In this way, by merely making an admixture in which the gas to be observed is quantitatively reduced, so that the lines which we wish to investigate are just visible in their thinnest state, we have a perfect means of doing this without any apparatus depending on the use of low pressures; and those who have worked most with Geissler tubes will appreciate the very great simplicity of work which is thus introduced.

Another important application of spectroscopic theory recently applied to the investigation of the chemistry of the sun is this:—Assume that the spectrum of any substance is not a pure spectrum of that substance, but of that substance as it generally exists in an impure state.

The spectrum will be found rich in lines; and when very considerable care is employed, one may go away with the idea that in iron, for instance, all the lines which are observed in the spectrum of iron coincident with Fraunhofer lines represent coincidences in the case of each line with iron in the sun and iron in our laboratory. But the more the work is carried on, the more one finds that the complex spectra which are observed are really much more simple when all the impurities are taken into account.

In the region of the solar spectrum, for instance, recorded on the map exhibited we have a great many iron-lines; but before the method of determining impurities was utilized, the spectrum was very much richer than it is at present; possibly one fourth of the lines have been withdrawn. In every specimen of iron which has been used in this work the lines of calcium, aluminium, and some of the lines of manganese and cobalt have been represented; and no chemist will wonder at this result. But there is a very curious thing which chemists, I think, will wonder at. In this part of the spectrum there were two lines which, by their thickness both in the solar and iron spectra, seemed undoubtedly to belong to iron; but further inquiry led to this extraordinary result—that one of these lines in all probability has its origin in the vibration of molecules of tungsten, the other being probably a line of molybdenum. Glucinum is another metal which may be referred to in this connexion; and it would appear that it is almost impossible to get a specimen of iron which does not contain, not only calcium and aluminium, but others which we consider rare metals on the earth, such as tungsten, molybdenum, and glucinum.

A few years ago, taking the work of Kirchhoff, Bunsen, Angström, and Thalén into consideration, and connecting it, so far as one could connect it, with those ideas of which recent eclipses have been so fruitful, our chemical view of the sun's atmosphere was one something like this:—We had, let us say, first of all an enormous shell of some gas, probably lighter than hydrogen, about which we know absolutely nothing, because at present none of it has been found here; inside this we have another shell, of hydrogen; inside this we have another shell, of calcium, another of magnesium, another of sodium, and then a complex shell the section of which has been called the reversing layer, in which we get all the metals of the iron group plus such other metals as cadmium, manganese, titanium, barium, and so on. The solar atmosphere, then, from top to bottom, consisted, it was imagined, of a series of shells, the shells being due not to the outside substance existing only outside, but to the outside substance extending to the bottom of the sun's atmosphere, and finding in it at a certain height another shell, which again formed another shell inside it, and so on; so that the composition of the solar atmosphere as one went down into it, got more and more complex: nothing was left behind; but a great many things were added.

The recent work, so far as I am acquainted with it, has not in any way upset that notion; but what it has done has been to add a considerable number of new elements to this reversing layer. Instead of consisting of 14 elements, as it was then found to do, it may be, I think, pretty definitely accepted now to consist of about thirty.

The metals considered to be solar as the result of the labours of Kirchhoff, Ångström, and Thalén together with the considerations brought forward regarding the length of the lines, were as follows:—

Na Fe Ca Mg Ni
Ba Cu Zn Cr Co
H Mn Ti Al

Those more recently added, with the evidence by which their existence in the solar atmosphere is rendered probable, are as follows (in the Tables, pp. 315–317).

It is important to bear in mind that the lines recorded in these Tables are in most cases the very longest visible in the photographic region of the respective spectra; in some cases they are limited to the region 39–40, which I have more especially studied; so that the fact of their being reversed

Metals the presence of which in the Sun is confirmed.

Name of metal.	Approximate W.L. of lines reversed in the solar spectrum.	Observations.	By whom previously mapped.	Particulars from Thalén's Tables.		
				Metal.	Wave-length.	Intensity. 1=brightest.
Strontium	4029·60	Absent from spectre normal, near long Mn line ...	New line.			
	4076·77	A line at 4076·9 in spectre normal assigned to Ca...	Thalén......	Sr .... Ca	4078·5 4077·0	1 3
	4215·00	In spectre normal assigned to Ca, W.L. 4215·40...	Thalén......	Sr .... Ca	4215·3 4215·3	1 1
	4607·50	A line at 4604·5 in spectre normal assigned to Ca	Thalén......	Sr .... Ca	4607·5 4607·5	1 4
Lead	4019·28	Absent from spectre normal	New line.			
	4056·80	An unassigned line near required position (W.L. 4057·25) in spectre normal	Thalén.........	Pb	4058·0	4
	4061·25	Absent from spectre normal	Thalén.........	Pb	4062·5	4
Cadmium	4677·00	An unassigned line at W.L. 4676·5 in spectre normal...	Thalén...... Kirchhoff...	Cd	4676·8	1
	4799·00	An unassigned line at W.L. 4798·9 in spectre normal	Thalén...... Kirchhoff...	Cd	4799·0	1
Potassium	4042·75	Absent from spectre normal	New line.			
	4046·28	Absent from spectre normal	New line.			
Cerium	3928·7	Absent from spectre normal	New line.			
	4012·0	Absent from spectre normal	New line.			
Uranium	3931·0	Absent from spectre normal	New line.			
	3943·0	Close to Al line	New line.			
	3965·8	Absent from spectre normal	New line.			

Metals probably present in the Sun.

Name of metal.	Approximate W.L. of lines reversed in the solar spectrum.	Observations.	By whom previously mapped.	Particulars from Thalén's Tables.		
				Metal.	Wave-length.	Intensity. 1 = brightest.
Vanadium	3901·3		New line.			
	3909·3		New line.			
	3989·65		New line.			
	3992·5		New line.			
	3997·9		New line.			
	4379·0	Assigned by Ångström to Ca	Thalén	Ca Va	4379·1 4379·0	4 1
	4384·0	Absent from Ångström's map	Thalén	Va	4384·0	1
	4389·0	Assigned by Ångström to Ca	Thalén	Ca Va	4389·4 4389·0	4 2
	4407·5	Assigned by Ångström to Ca	Thalén	Ca Va	4407·0 4407·5	5 1
Palladium	3893·0		New line.			
	3958·0		New line.			
	4787·0	Assigned by Ångström to Fe	Thalén	Pd Fe	4787·0 4785·8	3 5
	4817·0	Not allocated by Ångström	Thalén	Pd	4817·0	3
	4874·0	A line near required position assigned by Ångström to Fe	Thalén	Pd	4874·0	3
Molybdenum	3902·0	Very near Fe line	New line.			
	4576·0	Not allocated by Ångström	New line.			
	4706·0	Assigned by Ångström to Fe	Thalén	Mo Fe	4706·5 4706·5	4 5
	4730·0	Assigned by Ångström to Fe	Thalén	Mo	4730·5	4
	4818·0 ?	Absent from Ångström's map	Thalén	Mo	4818·0	4
	4829·0 ?	Line near assigned by Ångström to Ni	Thalén	Mo Ni Ni	4829·5 4828·4 4830·2	4 5 5

Metals probably present in the Sun (*continued*).

Name of metal.	Approximate W.L. of lines reversed in the solar spectrum.	Observations.	By whom previously mapped.	Particulars from Thalén's Tables.		
				Metal.	Wave-length.	Intensity. 1=brightest.
Indium	4101·0	Apparently coincident with Fe line in solar spectrum	Thalén.........	In	4101·0	1
	4509·0	Absent from Ångström's map	Thalén.........	In	4509·5	1
Lithium	4603·0	The line in Ångström's map is placed at W.L. 4601·7 and no metal assigned	Thalén.........	Li	4602·7	1
Rubidium	4202·0	The line in Ångström's map is placed at 4201·0 and made winging the adjacent Fe line	Thalén.........	Rb	4202·0	2
Cæsium	4554·9	Assigned by Ångström to Fe; no line in Thalén in this position	New line.			
	4592·0	Absent from Ångström's map	New line.			
Bismuth...........	4722·0	Absent from Ångström's map	Thalén.........	Bi	4722·0	1
Tin	4524·0	Not in spectre normal, a neighbouring Bi line at 4524·4 is shown	Thalén.........	Sn	4524·0	1
Lanthanum ...	3948·2	Not in spectre normal	New line.			
	3988·0	Not in spectre normal	New line.			
	3995·04	Not in spectre normal	New line.			
Glucinum	3904·75	Not in spectre normal	New line.			
Yttrium or Erbium	3949·6	Not in spectre normal	New line.			
	3981·8	Not in spectre normal	New line.			

in the solar spectrum must be considered the strongest evidence obtainable in favour of the existence in the sun of the metals to which they belong, pending the complete investigation of their spectra.

Where, however, there is only one line, as with Li, Rb, &c., the presence of these metals in the sun's reversing layer can, for the present, only be said to be probable. Neither must it be forgotten that, in addition to the long lines which a spectrum may contain in the red, yellow, or orange, long lines may exist in the hitherto unexplored ultra-violet region; so that the necessity for waiting for further evidence before deciding finally upon the presence or absence of such metals in the sun will be rendered obvious.

It will be thought remarkable that, if the long lines of such metals as lithium and rubidium are found in the photographic region of the spectrum, the long lines Li W.L. 6705, Rb W.L. 6205 and 6296 should have escaped detection.

To this it may be replied that, although these red lines may be apparently the brightest to the eye, it by no means follows they are the longest, since they are situated in a part of the spectrum which affects the visual organ more strongly than the photographic region does. It is possible also that the reasoning I have lately used in a paper communicated to the Royal Society, on the spectrum of calcium, may be applied in these cases.

Since a sensitized film is affected by some rays more strongly than by others, in determining the lengths of lines from a photograph it is not fair to compare together portions of the spectrum separated by too great an interval.

Furthermore, the fact of these red lines having been overlooked in the solar spectrum is not conclusive proof of their absence, inasmuch as this portion of the spectrum is both brighter and less refrangible, and a greater degree of dispersion would be necessary when prisms are employed to render visible faint dark lines which are easily detected in the photographic region.

At present, then, out of the fifty-one metals with which we are acquainted here, more than thirty are known to exist in the sun with more or less certitude. Now it was a very remarkable thing that although such metalloids as carbon and sulphur, iodine, bromine, and the like, had been very diligently searched for, no trace whatever had been found of them, giving any evidence that they existed together with the metals in these zones (these shells) to which I have referred.

Some years ago evidence was brought forward of the possible existence of the metalloids as a group outside the metals; and the evidence for this suggestion was of the following nature:—Independently of any questions connected with solar physics, I think all students of science now agree that the vapours of the various elementary bodies exist in different molecular states; if these different molecular states are studied by means of the spectroscope, perfectly different spectroscopic phenomena present themselves. If we use a large coil, we can drive every chemical substance with which we are acquainted, including carbon and silicon, into a molecular grouping competent to give us what is called a line spectrum, the spectrum with which we are most familiar when we use metals or salts of metals in the electric arc.

If, however, other conditions are fulfilled; if these bodies are not so roughly handled—if, in other words, we employ a lower degree of heat, or if we use electricity so that we get quantity instead of tension, then these line spectra die away altogether, and we have a spectrum, so called, of channelled spaces or flutings. Perhaps it will be convenient that I should throw one of these spectra on the screen, and point out exactly the difference to which I refer. I will first call attention to a line spectrum. Those lines are due to the vibrations of molecules of calcium and aluminium. The flutings which I now throw on the screen are perfectly different in appearance; in this case they have been produced by the vibrations of carbon at exactly the same temperature at which we get the line spectrum from aluminium and calcium.

Now, while we got these thirty-three metals to give us line spectra coincident with Fraunhofer lines, the only evidence (very doubtful evidence) of the existence of the metalloids in the sun at all, depended on the fact that, in the case of iodine and chlorine, some of the channelled spaces observed in their spectra at a very low temperature were imagined to be traced among the Fraunhofer lines in the spectrum of the sun. It is four years ago since evidence was gathered of a more conclusive kind in the case of carbon. The kind of evidence will be sufficiently indicated by throwing a comparison of the solar and carbon spectra on the screen. Below we have the bright flutings due to carbon-vapour; and above the solar spectrum this photograph includes a part in the ultra violet. When this negative is placed under a magnifying-glass, we find that most of the very delicate lines constituting the fluting in the bright portion have their exact equivalents among the Fraunhofer lines. This is the best-established piece of evidence, so far as I know, which seems to indicate that we have truly some of the metalloids present in the atmosphere of the sun by the coincidence of their spectra with the Fraunhofer lines. Further, carbon at all events exists under such conditions that its molecular structure is very much more complex than that of the metals in the reversing layer; and therefore it is probably withdrawn from the excessive heat of the lower region occupied by the reversing layer, which is competent, as we know from from other considerations, to drive even carbon and silicon into the line-stage, supposing carbon and silicon to be there.

This branch of the work to which I have just referred, a branch which enables us to say that such a temperature must exist in such and such a region of the solar atmosphere, depends, in the main, upon questions raised by the differences between the spectra of certain bodies in the sun and in our laboratories. If, for instance, one wishes to observe the coincidence between, let us say, iron and the sun, iron is placed in the electric lamp; its spectrum is photographed: side by side with it we have the spectrum of the sun also photographed; and, as a rule (I say as a rule; but this is not absolute in the case of such metals as iron), the intensity of the iron-lines which we get in our laboratories is equivalented by the intensity of the so-called iron-lines which we assume to exist in the spectrum of the sun. That is the great argument, in fact, for the existence of iron in the sun. But when we leave the iron group of metals, we find others in which this coincidence, this great similarity of intensity from one end of the spectrum to the other, is very considerably changed. We get in the case of calcium very thick lines of calcium corresponding with very thin lines in the sun, and we get thin lines of calcium corresponding with very thick lines in the sun. In fact, the two thickest lines which have already been mapped in the spectrum of the sun are lines due to calcium. If we photographed the spectrum of calcium with a very weak arc in that electric lamp, they would scarcely be visible at all. If, however, we pass from the tension of the arc to the tension which is obtainable with the use of a very large coil, then we can make the spectrum which we get artificially correspond exactly with the spectrum with which the sun presents us naturally; and the more we increase the tension (the larger the coil and the larger the jar we employ), the more can we make our terrestrial calcium vibrate in harmony, so to speak, with the calcium which occupies a very definite region in the atmosphere of the sun. Now this gives us this very precious teaching:—We know that the vapour of *calcium* occupies such and such a position in the sun; we know that to get the two things in harmony, as I said before, we must employ a very large induction-coil; and we know, again, that if we do employ a large induction-coil, all these beautiful flutings in the *carbon*-spectrum which have been thrown on the screen disappear utterly. That kind of carbon is no longer present in the reaction; but instead of it we have a new kind of carbon which is only competent to give us bright lines. We know, fourthly, that those bright lines do not exist reversed in the spectrum of the sun. Therefore the carbon must exist higher than the calcium, in a region of lower temperature.

In what I have said up to the present moment (and I have just touched very slightly on the physical side of the work, because I believe that in the future it will be most rich in teachings of the kind I have indicated), I must remind you that I have dealt solely with the Fraunhofer lines. Now it is knowledge ten years old, that if we observe the solar spectrum with that considerable dispersion which is now, I think, imperative if we are to do much good with it, there are bright lines in the ordinary solar spectrum side by side with the dark ones.

In a paper communicated to the Royal Society in 1868 I find these words:—"Attention has recently been drawn to certain bright regions in the ordinary spectrum." The position of these bright lines in the ordinary spectrum was then stated, and attention was called, among others, to one between *b* and

F. I call especial attention to that line now because the requisite amount of dispersion is now so common that any one, whenever the sun shines, may turn to *b* and see that bright line for himself. It will be found just as much outside the fourth line of *b* as the third line is on the other side of it. This bright line, lying in the most visible part of the spectrum, is exactly similar to many others, some of them in the yellow and some of them in the red. A careful list of these lines was made some years ago; and, I am sorry to say, the list was unfortunately lost by one of my assistants in a Metropolitan Railway-carriage; at all events, enough was said in this and other countries about these bright lines in the years 1869 and 1870 to have given rise, at all events, to the hope that any one interested in solar physics would be perfectly familiar with them. Among other matters which called attention to their existence was a correspondence which took place in the *Comptes Rendus* of the Academy of Sciences in Paris between Father Secchi and another observer in connexion with solar spots. I have remarked that a large dispersion is requisite to see these bright lines, because with a small dispersion bright regions of another kind in the solar spectrum are very obvious. When this small dispersion, however, is changed for a large one, one sees that these bright regions in the solar spectrum are due to the absence of fine lines; and, indeed, if one observes the solar spectrum with considerable dispersion through a cloud which prevents the fine lines from being seen, then there is a very considerable relative diminution in the intensity of some parts of the spectrum, and a very considerable relative increase in others, where these very fine lines are present and absent relatively, so as to give rise to the appearance of a very considerable change indeed in the background of the spectrum.

When, however, a very considerable dispersion is employed and photography is brought into play, if precautions be taken to give sufficient exposure, these bright regions, as opposed to the bright lines, entirely disappear. I have here, by the kindness of two friends, Mr. Rutherfurd and Captain Abney, the means of showing you exactly what I mean. A Rutherfurd grating containing 17,000 lines to the inch has been used as a means of obtaining the spectrum; and the film employed was kindly put on the plate for me by Captain Abney himself. We find, now, that Mr. Rutherfurd has given us an engine of such enormous power that the fineness of the collodion film is entirely distanced; that is to say, we can get from these perfect gratings spectra so extremely fine and so full of detail, that they can be enlarged until the structure of the ordinary collodion comes in and prevents a fine picture. But if instead of the ordinary collodion process, those which are being worked out with such success by Captain Abney be employed, then it appears that the film is as perfect a thing in its way as the grating is in its way, and one can go on obtaining any magnification one wants.

This is a photograph of the H lines obtained by the grating and film to which I have referred. Between the H and K lines, where the eye sees faintly three lines, there are now nearly a hundred; and that will speak more than any words of mine as to the extreme importance of the introduction of photography in such a research as this. Now here there are no bright lines; but, very conveniently, this next photograph contains one of the bright lines discovered and carefully recorded by Cornu, who has recorded bright lines in the ordinary solar spectrum as well as Hennessy. In exactly the middle of the field now is the bright line recorded as a bright line by Cornu in his map of the blue end of the solar spectrum; but excepting that one bright line, which is much more intense than any other part of the spectrum, bright lines are non-existent.

During the course of last year Dr. Draper, of New York, published the first results of a research which he has undertaken, going over very much the same ground with regard to the metalloids as had been gone over in this country with regard to the metals. Dr. Draper, who has long been known as a most earnest student of science, approached this subject with a wealth of instrumental means almost beyond precedent; and his well-known skill and assiduity, in the course of the two or three years during which his work was carried on, enabled him to accumulate facts of the very greatest importance. I am most anxious to make these preliminary remarks, and to state my very highest respect for Dr. Draper, because in referring to his work I shall have to point out that some of his results are, in my opinion, not yet completely established. Dr. Draper, in the first instance, claims the discovery of the bright lines already referred to, and bases a new theory upon them. It is by no means as a stickler for priority that I regard this as a very great pity, but because I think that, if the very considerable literature touching these bright lines (papers by Young, Cornu, Hennessy, Secchi, and others) had been before Dr. Draper when his paper was written, the necessity for the establishment of a new theory of the solar spectrum, which doubtless cost him very considerable thought, would probably have been less obvious.

Dr. Draper was so kind as to send me some little time ago a photograph of the solar spectrum confronted with the lines of oxygen; and the result which this photograph is claimed to show is, that a considerable number of the oxygen-lines are coincident with bright lines in the solar spectrum. I will throw this photograph of Dr. Draper's on the screen, in order that we may have common ground of thought. The lower part of the photograph gives the lines of oxygen; the middle part gives Dr. Draper's photograph of the sun, and the upper part a photograph of the sun taken in England, which I have put side by side with Dr. Draper's in order that the definition of the two photographs may be contrasted.

On examining the upper photograph with a very considerable magnifying-power, the detail comes out marvellously, and the spectrum between the more marked lines is found to be occupied with extremely fine lines in those regions where Dr. Draper's photograph gives ribbed structure, which, I fear, may not be due to the solar spectrum at all. In the silver-on-glass gratings, one of which Mr. Rutherfurd was so kind as to give me, I find that, in consequence of the grating being ruled on the back surface of the glass and the double transmission of the light through the plate, there is a considerable formation of Talbot bands, and the solar spectrum is in some regions entirely hidden and absolutely transformed. Lines are made to disappear; lines are apparently produced; so that if one compares a part of the spectrum taken with one of these silver-on-glass gratings with an ordinary refraction-spectrum, the greatest precaution is requisite. Indeed I think I am not going beyond the mark when I say that the positions of all lines below the third or fourth order of intensity must be received with very great caution indeed when these gratings are employed. So well is this known to Mr. Rutherfurd himself, who prepared these gratings for another purpose, that he is now, with equal generosity, distributing gratings containing the same number of lines to the inch (17,300, or something like that) engraved on speculum-metal in order that these defects may be obviated.

With regard to this work of Dr. Draper's, then, I wish to point out that the photograph in which these comparisons with the oxygen-lines have been made is not one which is competent to settle such an extremely important question. Secondly, upon examining these oxygen-lines, I do not find the coincidences to which he refers with bright solar lines and oxygen-lines in that part of the spectrum with which I am most familiar, for the reason that there are no bright lines whatever in this portion of the spectrum. I have here enlargements of negatives going nearly the whole length from G to H, one of the regions which are included in this photograph of Dr. Draper's. I have carefully gone over these regions line for line; and in no case do I see any bright line in the sun whatever coincident with any line of oxygen whatever. I cannot profess to have gone over the ground in the ultra violet; but it will appear to me very surprising indeed if, when we go further, when we include the H and K lines which have already been thrown on the screen, that Dr. Draper will find any possible coincidences with bright lines of the sun even there, because, when perfect instrumental conditions are brought into play, no bright line whatever exists in the part of the solar spectrum which is included in this map.

The bright line discovered by Cornu exists outside K; but between the region included in this map and the G lines I find no obvious bright line.

There is an experiment which any member of the Physical Society who possesses a spectroscope with three or four prisms can make for himself. Take the spark in air in an apparatus of the kind to which I have referred, use a comparison prism, flood the air with nitrogen, and in the field of view which includes *b* (and therefore one of the most marked bright lines in the solar spectrum itself) you will find three or four undoubted lines of oxygen. I have made that experiment, which is quite a simple one; and I find no coincidences in this part of the spectrum between any of these oxygen-lines and the undoubted bright lines. I have not tried it yet for the lower parts of the spectrum in the red and yellow, because I hope that Dr. Draper will try for himself.

I do not say that Dr. Draper's alleged discovery is no discovery at all; I say (and I think it is my duty to say it, as I have been occupied in closely allied work for some considerable time) that I do not hold it to be established.

I have no doubt that Dr. Draper will carefully go over his work himself; and I am quite certain that he will be the very first to hail what I have said today with satisfaction, because his desire, I am sure, is the desire of every true man of science, that the truth should prevail. In any case Dr. Draper has begun work in a branch of the chemical inquiry into solar matters which, up to the present time, has been sadly neglected; and we should all be grateful to him on that ground. I have no doubt that he on his side, as I on mine, hopes, as I said before, that the Physical Society of London and the Physical Societies of America will come forward and supply more workers for a branch of science which I am certain in the future will be regarded as one of very considerable importance.

XXXIII. *On the Discharge of Water from Orifices at different Temperatures.* *By* Professor W. C. Unwin, *M.I.C.E.*

In the Journal of the Franklin Institute for May 1878, there is a paper by Chief-Engineer Isherwood, of the U.S. Navy, giving an account of some experiments on the discharge of water from orifices at different temperatures. Those experiments appear to have been made on a sufficient scale and with very great care; and they lead to the conclusion that temperature has a very marked influence on the discharge. The author evidently supposes his conclusions to be applicable to orifices in general; for he remarks that, "in the various determinations which have been made of the ratio of the actual to the theoretical discharge of water through orifices, the temperature of the water should have been noted. The experimental ratios are true for only the experimental temperatures, and need reduction to a standard temperature."

The experiments were made by noting the time in which the level of the water in a cylindrical vessel fell from one level to another, the water being discharged from a given orifice. The observed results of the experiments are not given. These results were plotted in a diagram, and a fair curve drawn passing as evenly as possible through the plotted points. The results are stated to have been corrected for the dilatation of the orifice by heat; but it is not stated whether any correction was made for the dilatation of the volume of the vessel from which the water flowed, a correction quite as important as the other. The following short Table gives a few of Mr. Isherwood's results, as measured by him from the curve representing the observed results:—

Temperature, Fahrenheit. °	Relative time of discharge for equal volumes.	Relative velocities of discharge for equal volumes.
32	1·0000	1·0000
60	0·9896	1·0105
100	0·9696	1·0313
140	0·9457	1·0577
180	0·9156	1·0922
212	0·8855	1·1293

Thus the velocity of discharge increases 12 per cent. as the temperature rises from 32° to 212°, and it increases 8 per cent. as the temperature rises from 60° to 180°.

Now there is this difficulty in accepting the results of Mr. Isherwood's experiments,—that the actual velocity of discharge at ordinary temperatures differs from the whole velocity due to the head by only from 3 to 6 per cent. for simple orifices. It is not easy to see that any increase of fluidity of the water or diminution of friction could do more than annul this loss of from 3 to 6 per cent. Mr. Isherwood's experiments seem to imply that the velocity of discharge at high temperatures may be greater than the velocity due to the head. It seemed worth while therefore to repeat the experiment. The means at the author's disposal did not permit him to make the experiments on quite so large a scale as those of Mr. Isherwood; but it was, he believes, quite large enough to indicate any gain of velocity of the amount mentioned above.

A cast-iron cistern was used, the interior bored out to a diameter of 0·4 metre. The first orifice tried was a carefully formed brass conoidal orifice, formed as nearly as might be to the shape of the vena contracta, and very approximately 0·01 metre diameter. Three pointed indexes were fixed in the cistern, below the surface of the water; so that, as the level of the water descended, the instant at which the point broke the surface could be very exactly observed. Calling the levels of the three indexes A, B, and C, the time was noted in which the water-level descended from A to B and from A to C. A chronograph-watch was used, the seconds' hand being started at the moment the water-level was at A. When the level reached B, the time elapsed was noted by an observer counting seconds. When the level reached C the hand of the watch was stopped. This last observation was perhaps more reliable than the intermediate one at the level B.

For the higher temperatures the water was taken from a steam-engine boiler; it was somewhat discoloured by iron and sediment. The same water was used in the experiments at lower temperatures, but in its ordinary clean condition. The author does not think that the condition of the water made any sensible difference in the results of the experiments.

Experiments on a Conoidal Orifice, June 4, 1878.

Temperature, Fahrenheit.	Time of fall of water-level in seconds.	
	From A to B.	From A to C.
190°	59	89
190	58½	88½
130	59½	90
60	62	93
60	61½	92½

Mean Results.

Temperature, Fahrenheit.	From A to B.	From A to C.
190	58·75	88·75
130	59·5	90·00
60	61·75	92·50

These results show a distinct increase of velocity of discharge at the higher temperatures; but the increase from 60°

to 190° is only 4 per cent., or less than half the increase observed by Mr. Isherwood.

When water issues from an orifice with gradually diminishing head, the relation between the time and volume of discharge is given by the well-known equation

$$t=\frac{\Omega}{c\omega}\left\{\sqrt{\frac{2h_1}{g}}-\sqrt{\frac{2h_2}{g}}\right\}, \quad . \quad . \quad . \quad . \quad (1)$$

where Ω = area of water-surface in reservoir,
ω = area of orifice,
h_1, h_2 = heads at beginning and end of experiment above centre of orifice,
t = time of outflow in seconds,
c = coefficient of discharge.

Let D = diameter of the cylindrical reservoir, and d = diameter of the orifice. Then

$$\frac{\Omega}{\omega}=\frac{D^2}{d^2}.$$

Hence the equation above becomes

$$t=\frac{D^2}{cd^2}\sqrt{\frac{2}{g}}\{\sqrt{h_1}-\sqrt{h_2}\}.$$

In these experiments D = 15·7 inches, d = 0·3937 inch. Reducing these values to feet and introducing them in the equation,

$$t=\frac{394{\cdot}376}{c}\{\sqrt{h_1}-\sqrt{h_2}\}.$$

The heights of the index-points above the centre of the orifice were, as nearly as could be measured,

A	1·467 foot.
B	1·133 ,,
C	0·9775 ,,

Hence, for experiments in which the level fell from A to B,

$$c=\frac{57{\cdot}895}{t}\ ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for experiments in which the level fell from A to C,

$$c=\frac{87{\cdot}748}{t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Neglecting for the present the expansion of the reservoir and orifice, the coefficients of discharge deduced from the experiments are as follows :—

Coefficients of Discharge.

	Fall of level from A to B.	Fall of level from A to C.
190°	·9813 ·9896	·9859 ·9915
130°	·9730	·9750
60°	·9338 ·9414	·9435 ·9486

Mean Values of c.

190°	0·9871
130°	0·9740
60°	0·9418

The experiments on a conoidal orifice having shown a small but definite influence of temperature on the discharge, it seemed desirable to try whether a similar effect would be produced in the case of a thin-edged orifice. With the conoidal orifice there is no contraction of the jet, and the discharge is less than the so-called theoretical discharge by an amount depending only on the friction of the orifice. In the case of a thin-edged orifice, the jet contracts to an area of about $\frac{5}{8}$ that of the orifice; and the discharge is diminished not only by the friction, but also to a much greater extent by the contraction. The thin-edged orifice was 1 centimetre diameter; and the heads were nearly the same as before.

Experiments on Thin-edged Orifice, 1 *centim. in diameter,* June 12, 1878.

Temperature, Fahrenheit.	Time of discharge of water between A and B in fifths of a second.	Time of discharge of water between A and C in fifths of a second.
205°	503	748
205	500	747
140	507	744
65	500	746
61	495	740
61	495	740

Mean Values.

62°	496·6	742
140	507·0	744
205	501·5	747·5

The times here recorded show that, in the case of a thin-edged orifice, the temperature has an extremely small influence on the discharge, and that, unless the small differences in the experiments are errors of observation, the discharge is greater at low temperatures. Whether this is due to the increase of temperature increasing the contraction at the same time as it diminishes the friction, could only be determined by much more extensive experiments.

For these experiments, when the level fell from A to B,

$$c = \frac{292 \cdot 75}{t}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and when the level fell from A to C,

$$c = \frac{443 \cdot 71}{t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

t being in fifths of a second.

Coefficients of Discharge for Thin-edged Orifice.

Temperature, Fahrenheit.	Values of *c*. Fall of level from A to B.	Values of *c*. Fall of level from A to C.
205°	·5820	·5932
205	·5855	·5940
140	·5774	·5964
65	·5855	·5948
61	·5914	·5996
61	·5914	·5996

Mean Values.

Temperature, Fahrenheit.	Fall of level from A to B.	Fall of level from A to C.
205°	·5837	·5936
140	·5774	·5964
62	·5894	·5980

These results seem to show that the temperature has hardly any sensible influence on the discharge from orifices of this kind.

It will be seen that the results of these experiments do not at all agree with those of Mr. Isherwood; and although made on a smaller scale, the author believes that if the influence of temperature had been nearly as great as that stated by Mr. Isherwood, it could not possibly have escaped detection. Minute errors in measuring the head or the size of the orifice would sensibly affect the values of the coefficients obtained; and these may possibly be wrong to the extent of 2 or 3 per cent.; but these errors would not affect the relative values of the coefficients in any sensible degree, and the author therefore believes that temperature has a far less influence on the discharge from simple orifices than Mr. Isherwood's results would imply. It is difficult to explain to what the higher results obtained by Mr. Isherwood are due; but the conjecture may be hazarded that the orifice in his experiments was very exceptionally placed. It was at the end of a bell-mouthed tube some 10 inches long, a great part of which was only $\frac{3}{4}$ inch diameter; and there was a plug-cock immediately above the orifice. It seems possible that there was a good deal of friction in this pipe, and that the diminution of friction in this part of the apparatus led to the increase of discharge as the temperature increased *.

Thus far the effect of the temperature on the capacity of the reservoir and the size of the orifice has been neglected. It only remains to examine whether the expansion of these has any material influence on the results.

The effect of temperature on the quantities entering into the equation of flow is twofold. First, the ratio $\frac{D^2}{d^2}$ is altered, because the mouthpiece was of brass and the reservoir of cast iron; and the former expands more than the latter. Secondly, the level marks being attached to the side of the cistern, the distance between these marks and the centre of the orifice increases as the temperature rises. There is, however, an uncertainty in applying a correction for the expansion of the metal, because, ~~its~~ external surface being exposed to the air, its mean temperature would be less than the temperature of

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* It is impossible to calculate, except roughly, the frictional resistance of the tube to which, in Mr. Isherwood's experiments, the orifices were attached. Taking 4 inches length of pipe $\frac{3}{4}$ inch in diameter, and neglecting the bell-mouthed part, we get, using D'Arcy's coefficient of friction, and putting the data in feet:—

For a discharge of	0·0167	0·0374
„ velocity	5·5	12·2
„ head lost in pipe	0·6	0·12
„ total head	5·0	1·0

So that apparently about 12 per cent. of the head may have been lost in the friction of the pipe leading to the orifice.

the water. The following estimate of the correction is therefore approximate only.

Let e_b be the expansion of brass per unit of length and per degree;

e_c the expansion of cast iron estimated in the same way;

$\tau =$ the excess of temperature during the experiment reckoned from 60°.

Then, in consequence of the expansion of the metal, the ratio of the areas $\frac{D^2}{d^2}$ becomes

$$\frac{(1+e_c\tau)^2}{(1+e_b\tau)^2}\frac{D^2}{d^2},$$

and the true difference of the square roots of the heads is

$$\sqrt{1+e_c\tau}(\sqrt{h_1-h_2}).$$

The formula of flow, allowing for the alteration of the dimensions by rise of temperature, is therefore

$$t=\frac{(1+e_c\tau)^2}{(1+e_b)\tau^2}\sqrt{1+e_c\tau}\,\frac{D^2}{cd^2}\{\sqrt{h_1}-\sqrt{h_2}\}.$$

Let $e_c = {\cdot}000006$,

$e_b = {\cdot}00001$,

$\tau = 190° - 60° = 130$;

$$\frac{(1+e_c\tau)^2}{(1+e_b\tau)^2}\sqrt{1+e_c\tau}=\left(\frac{1{\cdot}00078}{1{\cdot}0013}\right)^2\sqrt{1{\cdot}00078}=0{\cdot}999355.$$

Hence it is obvious that the effect of the expansion of the reservoir and orifice is very small for the range of temperature in these experiments. Allowing for that expansion, we get for the experiments at 190°,

$$c=\frac{{\cdot}99935\,D^2}{td^2}\{\sqrt{h_1}-\sqrt{h_2}\},$$

or slightly smaller values of the coefficient than those given above.

It is rather curious that it is stated in Mr. Isherwood's paper that the results are corrected for the variation of the size of the orifice as the temperature varied, but no mention is made of a correction for the size of the reservoir or the expansion of the vessel to which the index-marks denoting the initial and final heads were attached. If these latter corrections have

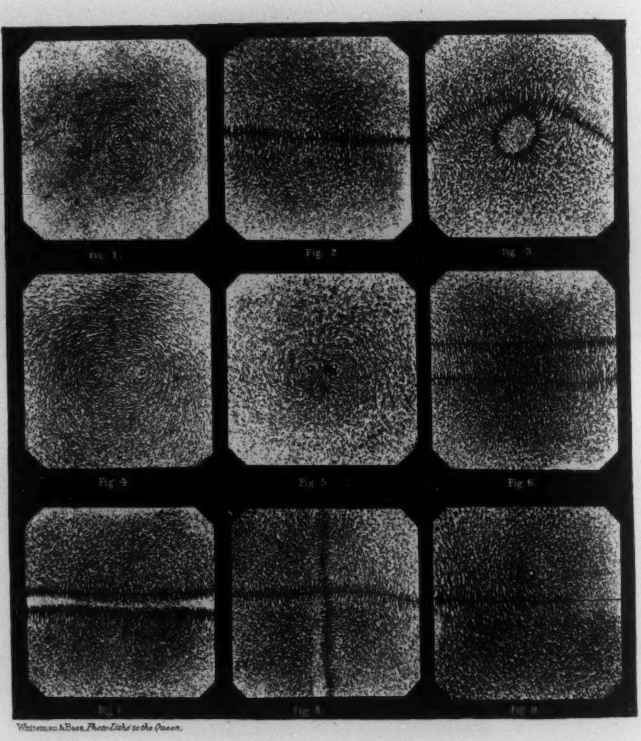

Fig. 1. Fig. 2. Fig. 3.

Fig. 4. Fig. 5. Fig. 6.

Fig. 7. Fig. 8. Fig. 9.

Whiteman & Bass, Photo-Lith^s to the Queen.

MAGNETIC FIGURES
ILLUSTRATING ELECTRO-DYNAMIC RELATIONS.

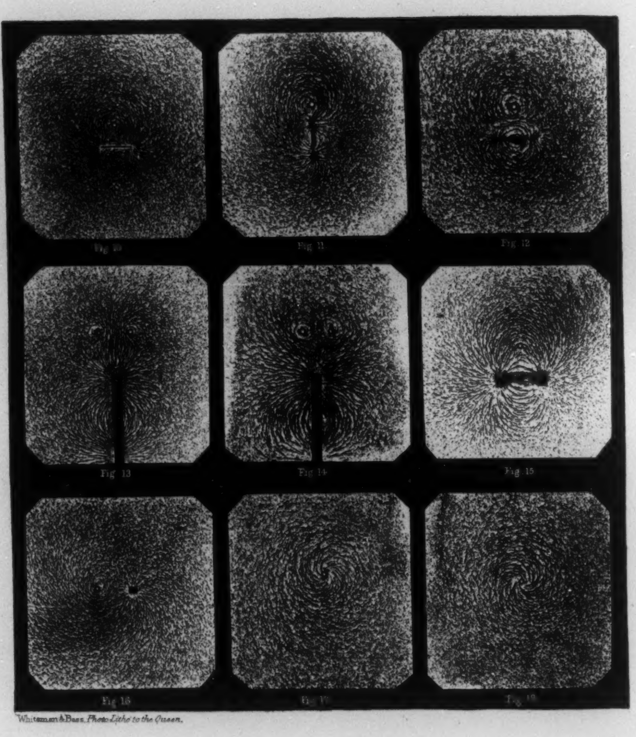

Fig. 10 Fig. 11 Fig. 12

Fig. 13 Fig. 14 Fig. 15

Fig. 16 Fig. 17 Fig. 18

Whiteman & Bass, *Photo Litho' to the Queen.*

MAGNETIC FIGURES

ILLUSTRATING ELECTRO-DYNAMIC RELATIONS.

been omitted, though this is difficult to believe, Mr. Isherwood's results should be divided by

$$(1+e_c\tau)^2\sqrt{1+e_c\tau},$$

where e_c is the coefficient of expansion of the material of the reservoir, whatever that was. This would sensibly diminish the apparent increase of discharge at high temperatures given in his experiments.

XXXIV. *Magnetic Figures illustrating Electrodynamic Relations.* By SILVANUS P. THOMPSON, *D.Sc., B.A., F.R.A.S., Professor of Experimental Physics in University College, Bristol.*

[Plates VIII. and IX.]

IN a preliminary communication to the Physical Society in February of the present year, the author announced a method of studying and illustrating the known laws of the mutual attractions or repulsions of conductors traversed by electric currents. The present paper is a complete statement of the facts obtained in the experimental research which formed the basis of that communication.

While preparing a set of magnetic currents to illustrate the mutual actions of magnet-poles, it occurred to the writer that the mutual attractions and repulsion of currents might be illustrated in a similar manner by the figures formed with iron filings. He was aware* at that time that the lines of force of a straight conductor carrying a current were a series of concentric circles lying in a plane to which the conductor was normal. The series of figures now published originates, therefore, with the discovery of Faraday that the seat of the mutual actions of currents and of magnets must be sought in the surrounding medium. Since the communication of the preliminary notice, the writer has learned that one or two of the figures had been previously and independently observed by Professor

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* See Faraday, 'Experimental Researches in Electricity,' vol. iii. p. 400, § 3239, and plate iii. fig. 17; Guthrie, 'Magnetism and Electricity,' p. 254, fig. 225; Clerk-Maxwell, 'Electricity and Magnetism,' vol. ii. art. 477.

F. Guthrie, but not published. Two others, Nos. 4 and 5 of the present series, are imperfectly given by Faraday in figures 18 and 19 of plate iii. in the third volume of his 'Experimental Researches' (Series Twenty-ninth)*, and without reference to the conclusions to be derived from their forms, which Faraday apparently overlooked †.

The method employed for preserving the figures has been uniform throughout the series. Plates of glass, 3½ inches long by 3¼ inches broad, were coated with a solution of gum-arabic and gelatine, and were then carefully dried. When the arrangement of magnets or of conducting-wires had been made for the particular case of the experiment, and the plate been laid in a horizontal position, fine filings of wrought iron previously sifted were dusted over the plate through muslin, and the plate was tapped lightly with vertical blows from a piece of thin glass rod. When the filings had arranged themselves, and the plate was still *in situ*, a gentle current of steam was allowed to play upon the plate, condensing upon the surface of the gum and softening it, and thus allowing the filings to embed themselves where they lay. After the gum had again become hard, the prepared face was covered by a protecting plate of glass, on which in certain cases were drawn the positions of the wires or magnets employed. The figures fixed in this manner are suitable for projection with the lantern upon the screen. They can be readily photographed for transparencies, or for paper prints; specimens of each of these methods of photographic reproduction are exhibited to the Society.

Figure 1 represents the condition of the magnetic field surrounding the current in a straight conducting-wire, which was carried vertically through a hole drilled in the plate. The wire employed throughout the series was a silver one of about ·8 millim. in diameter. The battery power employed for this experiment was that of 20 Grove's cells arranged in two series of ten each. In some of the succeeding experiments a less current was found sufficient.

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* And 'Phil. Trans. 1852, p. 137.

† The attention of the writer has also been drawn to a statement in the American Journal of Science for 1872, p. 263, by Professor A. M. Mayer, that he has obtained magnetic "spectra" from electric currents in a manner somewhat similar to that now described. The figures have, however, remained unpublished and undescribed, so that the writer has no means of learning how far the substance of the present communication may have been anticipated.

But for the imperfections of the method of experiment, these curves would be perfect circles, and the distances between two successive lines of force would be proportional to the square of the distance from the central point. The equipotential magnetic surfaces, being always normal to the magnetic lines of force, would be represented by a system of radial lines forming equal angles with one another. There appears to be no recognized name for the closed curves traced out by the lines of force around conductors carrying currents. With great diffidence I therefore beg to speak of them as isodynamic lines. They are theoretically disposed about a single straight conductor in a perfectly concentric manner, and at such distances apart as would be defined by the requirement that a parallel conductor, carrying a like current of unit strength, would do unit work in passing from one isodynamic line to the next. The absolute value of an isodynamic line would of course be determined (like magnetic and electrostatic potential) by the work done by a like element of current in passing to any point in that line from an infinite distance. No work is done in moving an element of a parallel current along an isodynamic line, just as no work is done in moving a magnet-pole along in an equipotential surface. The isodynamic lines occupy, therefore, exactly the same relation to the element of the circuit, as do the equipotential surfaces to a magnet-pole or to an electrified point.

Figure 2 represents the field above a horizontal wire carrying a current, and separated from the filings by the thickness of the glass (about 1·7 millim.). The lines cross the wire at right angles, and are really the projections of a series of such circles as exist in figure 1.

Figure 3 exhibits the form assumed by the filings when the wire beneath the plate was coiled into a simple loop, a small piece of mica being inserted to prevent contact where it recrossed its path. The lines of the field within the loop run longitudinally; and their projections on the surface are mere points, as the filings show.

In figures 4 and 5, two wires pass vertically through the plane of the figures, carrying parallel currrents, which in figure 4 are in the same direction, in figure 5 in opposite directions. Ampère's well-known law of the attraction in the former case, and of the repulsion in the latter, is well illustrated by the forms of the magnetic curves. In the former, where the parallel currents attract, the outer isodynamic lines are closed curves embracing both centres, the inner are distorted ovals about each centre—the whole forming a system of lemniscates, as would necessarily be the case, since the attraction at any point in the plate varies inversely as the square of the distance from each current*.

In figure 5, where the parallel currents repel each other, the lines of force due to either current in no case enter or coalesce with those of the other current. They form two series of ovals of a peculiar form, flattened on the sides presented towards the opposing series.

The conception of Faraday, "that the lines of magnetic force tend to shorten themselves, and that they repel each other when placed side by side," has been shown by Clerk-Maxwell, who thus concisely states it, to be perfectly consistent with the theory that explains electromagnetic force as the result of a state of stress in the medium filling the surrounding space†. Faraday also observes that "unlike magnetic lines, when end on, repel each other, as when similar poles are face to face," and that "like magnetic lines of force," when end on to each other, coalesce. The terms "like" and "unlike," as applied to magnetic lines of force, refer, of course, to the two cases of similarly or oppositely directed lines, the positive direction of a line of force being reckoned as the direction in which a north-seeking pole on it would tend to move‡. The mutual coalescence or repulsion exerted between the lines of force of unlike or like magnetic poles is familiarly employed in the experimental illustration of magnetic phenomena, so well known since the researches of Professor Robison and Dr. Roget on the magnetic curves, and appears to have been recognized long before*. It is believed that the present is the first distinct attempt to apply similar considerations to the illustration of electrodynamic relations between systems of conductors carrying currents, and between conductors of currents and magnet-poles.

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* See Thomson and Tait, 'Natural Philosophy,' art. 508, vol. i. p. 382.

† Clerk-Maxwell, 'Electricity and Magnetism,' vol. ii. art. 645; Faraday, 'Experimental Researches,' 3266, 3267, 3268.

‡ See Clerk-Maxwell, 'Electricity and Magnetism,' art. 489; L. Cumming, 'Theory of Electricity,' p. 194.

The isodynamic lines, which are lines of magnetic force, tend to shorten themselves. A very hasty inspection of fig. 4 will show that if any one of the system of lemniscates were to "shorten itself," it would tend to bring the two centres nearer together. Consider each isodynamic line as a ring of some elastic material (as, for example, an indiarubber ring) stretched around a bundle of smooth wires, the cross section of the bundle having a perimeter corresponding in form to the isodynamic line under consideration. The maximum shortening of such an elastic ring would take place when the enclosed area was made a circle. In other words, the lemniscate-form isodynamics tend to become circles, and the two like parallel currents are mutually urged towards each other.

In figure 5 the shortening of the isodynamic lines, and their approach to the truly circular form, could only be accomplished by the wider separation of the two conductors from each other. Hence the mutual repulsion of two parallel conductors carrying oppositely directed currents.

Figures 6 and 7 show the lines of force above the parallel currents when these pass horizontally below the glass. In the case of like currents the lines coalesce. In the case of unlike currents they repel each other, and pass between the two wires in a direction vertical to the plane of the glass, where their characteristic form, as lines, is lost. The observation that the filings adherent to wires carrying like parallel currents are mutually attractive appears to have been first made by Davy.

Figure 8 illustrates the law of currents crossing one another at a point. In the two quadrants in which the currents both run to or from the central point, the lines of force tend to coalesce. In the alternate quadrants they mutually repel each other; and the angle of these quadrants tends to increase.

In figure 9 one current is carried horizontally below the glass, the other traverses the plane of the figure normally. The dissymmetry of the resultant distribution of the lines reveals the dissymmetrical nature of the force which tends to bring the currents into parallelism. Any shortening of the isodynamic lines would tend to move the vertical current from that quadrant over which the lines are unbroken. Figures have also been obtained with two currents crossing the plate in a vertical plane of incidence, but each at 45° to the normal. With some distortion, these figures bear a general resemblance to figs. 4 and 5 in the two cases of the currents passing through the plate in similar or in opposed directions. In the former case their angular separation tends to diminish, in the latter to increase.

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* See Musschenbroek, *Dissertatio Physica Experimentalis de Magnete*; cap. iv. exp. cxvii., and tab. iv. figs. 4 & 5.

Figures 10, 11, and 12 introduce the action of a vertical current upon a small magnetic needle lying on the glass plate. In the first case the needle lies in stable equilibrium almost tangentially to the isodynamic lines; in the third its position is reversed and unstable; in the second case it is set at right angles to the directive action of the current. The dissymmetrical action of the forces on its poles produces a couple tending to turn it about its centre, as would be inferred from an inspection of the lines of force of the figure.

Figures 13 and 14 illustrate a deduction from the theory of the magnetic shell. A conductor carrying a current is acted upon by a force urging it forward so as to make the number of like lines of force included within it a maximum*; that is to say, a north-seeking pole is attracted into a circuit on the side from which the positive current appears to circulate in a right-handed cyclical order (or in the same direction as the hands of a clock). Similarly the circuit is urged backwards from a contrary pole, and tends to make the number of unlike lines of force included within it a minimum. In the figures a current ascends through the plane of the figure on the left, and descends through it on the right, in a right-handed cyclical order as seen from the magnet. Hence a north-seeking pole is attracted, and a south-seeking pole repelled.

Figure 15 results from the action of two magnet-poles upon a vertical conductor, which in this case is attracted between the poles.

* Clerk-Maxwell, 'Electricity and Magnetism,' art. 490.

Figure 16 illustrates the mutual tendency to rotation between a magnet-pole and a conductor carrying a current parallel to the axis of the magnet. In the figure, where the vertical current passes upwards through the glass, the neighbouring south-seeking pole (marked in position by a square dot) is urged round the current with a couple tending in a right-handed cyclical rotation. The couple is reversed, and acts in a left-handed order, if either the current or the magnet-pole be reversed. The contrasted dissymmetry so produced is very curious, and the mutual displacement of the radial lines of force of the pole and of the circular lines of the current is very significant.

Figures 17 and 18 show lines of force arranged spirally in the field. In these a current passes upwards through the glass, while the pole of a magnet is placed vertically beneath: the current, in fact, passes through the magnet. The form of the lines of force is remarkable. No work would be done on or by an element of a vertical current in bringing it up to the centre along one of the spiral lines; for the work done *by* it in bringing it in the spiral path across the successive circular isodynamic lines of the current would be equal to that done *upon* it in carrying it across the successive radial lines of force of the magnet-pole. The equipotential surfaces of this field are consequently another series of spirals of an opposite cyclical order. In figure 17 the current running up through a south-seeking pole produced a right-handed spiral; in figure 18, with a north-seeking pole the spiral is of the opposite order. Since the magnetic potential decreases from a magnet-pole with the inverse square of the distance, and since the inductive action of the current on a point in the plane of the figure also decreases according to the inverse square of the distance from the current, each branch of the spirals would be described by a moving point whose angular displacement from the arbitrary zero is simply proportional to the distance from the central point. The results of actual measurement of the spirals at successive distances of whole millimetres from the centre show as near an agreement with this supposition as the roughness of the method of procuring the curves permits. The number of branches of the spiral will clearly be proportional to the strength of the magnet pole. The obvious result of a "shortening" of the spiral lines would be to produce a rotational movement, such as we know to be produced on a free-magnet pole under the influence of a current traversing it longitudinally.

I am indebted to Mr. Robert Gillo, of Bridgwater, for the admirable photographic copies of the various figures.

June 19, 1878.

XXXV. *On the Light reflected by Potassium Permanganate.*

By Sir JOHN CONROY, *Bart., M.A.*

THE light reflected from the surface of potassium permanganate was originally examined by Haidinger, who announced (*Sitzungsberichte der kaiserlichen Akademie der Wissenschaften*, Band viii. 1852, p. 133), that when the light reflected from the surface of the crystals and of the substance rubbed on a plate of glass was examined with a dichroiscopic lens, the portion polarized in the plane of incidence was light yellow at low angles, and became white as the angle increased, whilst the portion polarized perpendicularly was light yellow, and became green and blue as the angle increased.

Professor Stokes found (Phil. Mag. vi. 1853, p. 400) that the reflected light contained four bright bands, corresponding in position to the dark bands of the absorption spectrum of a solution of the substance, and that when the reflected light was separated into two streams polarized in, and perpendicular to, the plane of incidence, and then examined by a prism, the bands were hardly visible in the one, and the other at a certain angle consisted mainly of them.

E. Wiedemann has recently published (Pogg. *Ann.* cli. 1874, p. 625) an account of some experiments he has made on the same subject. He found that whilst the dark bands of the reflection spectrum did not even partially cover those of the absorption spectrum, they did not lie exactly intermediate between any two of them—and, further, that the position of the bands was independent of the angle of incidence, both with ordinary light, and with that polarized in the plane of incidence; but with light polarized perpendicularly to this plane, the bands occupied the same position up to a certain angle, and then with a slight increase of the angle suffered sudden displacement towards the blue, and a new band appeared near D. He also found that with light polarized perpendicularly to the plane of incidence, the position of the bands was independent of the nature of the surrounding medium, being the same when the permanganate was in air, benzene, and bisulphide of carbon; but when the light was polarized in the plane of incidence, with the increase of the refractive index of the medium the bands were more and more displaced towards the blue.

For some experiments I have made on the same subject I have used a Babinet's goniometer, which has, in addition to the ordinary horizontal stage, a vertical one so arranged that the reflecting surface can be placed over the axis of the instrument. Sunlight was used, which could be polarized in any plane by a Nicol supported by the fixed arm of the goniometer; and a small direct-vision spectroscope, by Hilger, with a "bright-point" micrometer and a reflecting prism for bringing a second spectrum into the field, was carried by the other arm of the goniometer. By placing a beaker on the horizontal stage, and, after the surface of the permanganate had been properly adjusted, filling it with the liquid and limiting the incident beam by a narrow vertical slit, the light reflected from the surface of the substance when immersed in a liquid could be examined.

The experiments were usually made with potassium permanganate crushed, and burnished with an agate on a piece of finely-ground glass; and it was found that the light reflected from the surface of crystals and from that of the substance rubbed on glass was identical; except that the blue rays were more intense in the light reflected by the crystals, and the higher bands were more distinctly seen.

The surface-colour of potassium permanganate, and the position and intensity of the bands in the spectrum of the reflected light, are independent of the relative position of the plane of incidence to the long axis of the crystal, or to the striæ produced by rubbing, when the powdered substance burnished on glass is used.

1. *Surface-Colours.*—Freshly prepared surfaces of potassium permanganate appear of a pale yellow when light, either unpolarized or polarized in any plane, is incident upon them

at low angles. But with ordinary light, and with light polarized in the plane of incidence, the amount of white light reflected is so great at high angles that the surface-colour, if any, is completely masked.

When the incident light is polarized perpendicularly to the plane of incidence, or when unpolarized light falls on the surface and a Nicol is placed between the eye and the permanganate, with its principal section in the plane of incidence, the surface-colour is seen to change as the angle increases, becoming successively green and blue, and finally white and metallic.

The surface-colours alter with the surrounding medium. The following Table gives, approximately, the colour at various incidences, (A) when the light is either unpolarized or polarized in the plane of incidence, and (B) when it is polarized perpendicularly to that plane, for potassium permanganate in air, tetrachloride and bisulphide of carbon.

Angle of incidence.		Surrounding medium.		
		Air.	Tetrachloride of carbon.	Bisulphide of carbon.
30°.	A	Pale yellow.	Yellow-green.	Yellow-green.
	B	,, ,,	,, ,,	Green.
35.	A	Pale yellow.	Yellow-green.	Yellow-green.
	B	,, ,,	,, ,,	Green.
40.	A	Pale yellow.	Yellow-green.	Yellow-green.
	B	,, ,,	Green.	Green.
45.	A	Pale yellow.	Yellow-green.	Yellow-green.
	B	,, ,,	Green.	Blue-green.
50.	A	White.	Yellow-green.	Yellow-green.
	B	Pale yellow.	Bright green.	Blue-green.
55.	A	White.	Green.	Yellow-green.
	B	Yellow, with a green tinge.	Blue-green.	Blue-green.
60.	A	White.	Green.	Green.
	B	Brilliant green.	Blue-green.	Blue-green.
65.	A	White.	Green.	Green.
	B	Blue-green.	Blue-green.	Blue-green.
70.	A	White.	Greenish.	Greenish white.
	B	Blue.	,,	,, ,,
75.	A	White.		
	B	Metallic, with blue shade.		

2. *Reflection Spectra.*—With unpolarized light, and still more with light polarized in the plane of incidence, the dark bands in the spectrum of the reflected light are never very distinct. I was not able to observe whether the bands shifted or not as the angle of incidence increased, as the amount of white

light reflected at angles of 55° and upwards was so great as to render the bands invisible. They appeared, however, as long as they were visible, to coincide exactly with the bright spaces in the absorption spectrum of a dilute solution of potassium permanganate, which was thrown into the field by means of the reflecting prism.

When the incident light is polarized perpendicularly to the plane of incidence, the dark bands are far more distinctly seen. At angles of less than 40° there are four bands, and the blue end of the spectrum is very weak. As the angle of incidence increases, the intensity of the blue rays diminishes; and then the amount of light in the red decreases; and at about 55° nearly the whole of the light comes from the bright bands.

As the angle of incidence increases beyond this amount, the dark bands gradually move towards the blue end of the spectrum; and at about 60° a new band appears near D. With any further increase of the angle more of the blue rays are reflected; and the bands fade away, those in the more refrangible part of the spectrum disappearing first. The relative intensity of the dark band varies with the angle of incidence. When this is small, the third and fourth bands, counting from the red end, are darkest; with the increase of the angle the second, the first, and finally the new band, become successively darkest.

I have not been able to obtain any satisfactory measurements of the amount of the displacement of the bands, as, when a spectroscope of sufficient power to render it an easily measurable quantity is used, the bands become so ill-defined that it is impossible to measure them. Approximately the displacement amounts to about 60° in "tenth-metres;" and the bands tend to coincide with the dark bands of the absorption spectrum, instead of with the bright bands as they do when the angle of incidence is about 55° or less.

The shaded portions of the diagrams are intended to give the relative amount of light, as determined by eye estimations, in the different portions of the absorption and reflection spectra of potassium permanganate—the ordinates being taken to represent the intensity, and the abscissæ wave-lengths. The curved line gives the intensity of the light in the different portions of the normal spectrum, as determined by Mossotti* from Fraunhofer's measurements, neglecting the minor irregularities in the curve as given by him.

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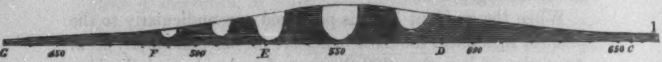
* Pogg. *Ann.* lxxii. p. 509.

Fig. 1 is the absorption spectrum of a solution of potassium permanganate in water.

Figs. 2, 3, and 4 the reflection spectra, when the incident light is polarized perpendicularly to the plane of incidence, and falls on the surface at angles of 50°, 60°, and 70°.



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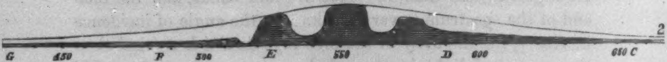

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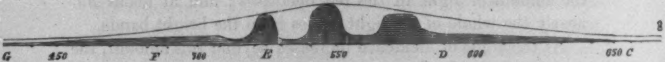

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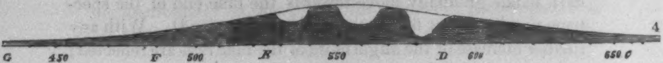

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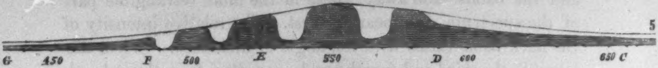

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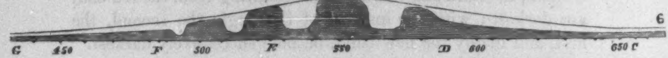

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As has already been announced by Wiedemann, the position of the bands in the reflected light depends on the nature of the surrounding medium. From the experiments I have made, it appears that, with unpolarized light, the first dark band of the reflection spectrum corresponds in position with the first bright band of the absorption spectrum, whether the permanganate is in air, benzene, or either bisulphide or tetrachloride of carbon; these liquids, however, act on the permanganate, and after a short time the surface becomes altered, and then the bands correspond with the dark bands of the absorption spectrum.

Figs. 4 and 5 represent the distribution of light in the spectrum, with fresh surfaces of potassium permanganate in bisulphide and tetrachloride of carbon, when unpolarized light is incident upon them at an angle of about 55°: in both cases the bands are wider apart than in air.

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PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1877-78.

Ordinary Meetings.

February 3rd, 1877.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

J. Norman Lockyer, F.R.S.

Hon. Members: A. Cornu; P. J. C. Janssen.

The following paper was read:—

"On Vortex Motion." By Prof. Osborne Reynolds.

February 17th, 1877.

Prof. W. G. Adams, F.R.S., Vice-President, in the Chair.

The following was elected a Member of the Society:—

T. W. Philips.

The following papers were read:—

"On Apparatus to illustrate Wave-motion." By C. J. Woodward.

"On Galvanometers in the form of Lantern-slides." By S. P. Thompson.

"On the Vapour-tension of Combined Water." By Dr. F. GUTHRIE.

"On the Distribution of Electricity in Non-conductors." By Dr. F. GUTHRIE.

March 3rd, 1877.

Prof. G. C. FOSTER, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

P. LE NEVE FOSTER, M.A.; J. A. FLEMING.

The following papers were read:—

"On the Polarization of Heat." By Prof. G. C. FOSTER.

"On an Arrangement of Thomson's Galvanometer for showing Small Deflections to an Audience." By LATIMER CLARK.

"On a Modified Form of the Holtz Machine." By W. J. WILSON.

March 17th, 1877.

Prof. G. C. FOSTER, F.R.S., President, in the Chair.

The following was elected a Member of the Society:—

W. S. SEATON.

The following papers were read:—

"On the Stratifications in Vacuum-tubes." By W. SPOTTISWOODE.

"On a Modification of Mance's Method for determining the Resistance of a Galvanic Battery." By O. J. LODGE.

"On the Theory of the Photographic Image." By Capt. ABNEY.

April 14th, 1877.

Prof. G. C. FOSTER, F.R.S., President, in the Chair.

The following papers were read:—

"On a Portable Calorimeter." By Dr. E. J. MILLS.

"On a New Half-prism Spectroscope." By W. H. M. CHRISTIE.

April 28th, 1877.

Prof. G. C. FOSTER, F.R.S., President, in the Chair.

The following papers were read:—

"On Selective Absorption." By W. ACKROYD.

"On the Composition of Rectangular Motions, and on a Method of Measuring the Velocity of Machinery." By Prof. McLeod.

May 12th, 1877.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

Capt. R. G. Scott, R.E.; Dr. Frankland, F.R.S.; W. H. M. Christie, M.A., F.R.A.S.; Lieut. Darwin, R.E.; Capt. Armstrong, R.E.; H. F. Morley, B.A.; A. Weiss.

The following papers were read:—

"On the Achromatism of the Eye in reference to the Perception of Distance." By S. P. Thompson.

"On the Acoustical Phenomena accompanying the rapid rotation of a Vibrating Tuning-fork." By S. P. Thompson.

May 26th, 1877.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

W. T. Thiselton Dyer, M.A., B.Sc.; Dr. H. Debus, F.R.S.; Lieut.-Col. Campbell, of Blytheswood; Capt. G. Sale, R.E.; William Jack, M.A.

The following papers were read:—

"On a Divided-Slit Spectroscope." By Lieut.-Col. Campbell.

"On Ice as an Electrolyte." By Profs. Ayrton and Perry.

June 9th, 1877.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

W. H. Northcott; L. J. Whalley.

The following paper was read:—

"On the Interference Fringes in a Nicol's Prism." By S. P. Thompson.

June 23rd, 1877.

Prof. G. C. **Foster**, F.R.S., President, in the Chair.

The following papers were read:—

"On the Adaptation to Clifton's Optical Bench of Melloni's Apparatus, and on an Arrangement for showing the Interference of Light by Thick Plates." By Prof. W. G. **Adams**.

"On the Electrical Diagnosis of Metals." By Dr. **Guthrie** and W. **Ackroyd**.

November 3rd, 1877.

Prof. G. C. **Foster**, F.R.S., President, in the Chair.

The following was elected a Member of the Society:—

A. **Jesseman**.

The following papers were read:—

"On Experiments to determine the Exact Number of Vibrations of Tuning-forks by means of the Apparatus already exhibited to the Society." By Prof. H. **M'Leod**.

Exhibition of Artificial Gems recently prepared by M. Feil. By Dr. **Huggins**.

"On Ice as an Electrolyte." (Continued.) By Profs. **Ayrton** and **Perry**.

"On a Simple Apparatus for showing the Interference of two Plane Waves." By Dr. F. **Guthrie**.

November 17th, 1877.

Dr. W. H. **Stone**, Vice-President, in the Chair.

The following paper was read:—

"On a Simple Form of Guard-ring Electrometer for Absolute Measurements." By Prof. G. C. **Foster**.

December 1st, 1877.

Prof. G. C. **Foster**, F.R.S., President, in the Chair.

The following paper was read:—

Lecture on the Telephone. By Prof. A. **Graham Bell**.

December 15th, 1877.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

J. W. Clark; J. M. Cameron; H. N. Moseley, M.A., F.R.S.; The Rt. Hon. Lord Rayleigh, M.A., F.R.S.; H. T. Wood; W. N. Stocker, M.A.; Prof. W. E. Ayrton; J. E. Judson, B.A.

The following papers were read:—

"On Permanent Plateau's Films." By S. P. Thompson.

"On the Colours exhibited by Vibrating Soap-films." By Sedley Taylor.

January 19th, 1878.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following were elected Members of the Society:—

Lieut. G. S. Clarke, R.E.; J. F. Iselin, M.A.; J. Angell; J. W. Russell, M.A.

The following papers were read:—

"On the Physical Theory of the Telephone." By W. H. Preece.

"On a Method of Measuring the Absolute Thermal Conductivity of Rare Substances." By Dr. O. J. Lodge.

Annual General Meeting.

February 2nd, 1878.

Prof. G. C. Foster, F.R.S., President, in the Chair.

The following Report of the Council was read by the President:—

The Council is again able to view with satisfaction the position and prospects of the Society.

The number of Members has risen from 201 at the date of the last Annual Meeting to 232 at the present time.

The papers and communications submitted to the Society have been nearly as numerous as in 1876. In the past year, however, the Society owes no less than nine of the thirty-five papers to the energy of two of its Members; and although the Council is not unmindful of the value and interest of the subjects brought forward, it would strongly urge that the continued success of the Society must in a great measure depend on the active support of each individual Member.

The Society is aware that the Council have undertaken, with the sanction of his representatives, to publish a collected edition of the scientific papers of the late Sir Charles Wheatstone. The printing of the papers is now approaching its completion, and the Council has pleasure in communicating to the Society the following Report presented to them by the Committee charged with superintending the publication:—

"*Report of the Committee for Reprinting Sir Charles Wheatstone's Papers.*

"The Committee have the satisfaction of reporting to the Council that this work is now nearly finished. Eighteen sheets are in type, and the remaining matter, amounting to three or four sheets more, is now in the hands of the printer.

"The Committee found much greater difficulty than they expected in obtaining copies of some of the papers; and owing mainly to this circumstance the work has occupied a much longer time than it was expected to take. The Committee, however, hope to be able to issue the volume very shortly."

It was resolved that a circular notice, embodying a proposal from the Council with reference to the translation of papers and monographs which have appeared in Foreign Journals, should be sent to each Member of the Society, and to certain other persons who might also afford valuable information and advice.

The subjoined Report has been presented to the Council in relation to the replies elicited by this circular, and is now communicated to the Society:—

"*Report of the Committee on proposed Reprinting of Scientific Papers.*

"The following circular was sent out to all the Members of the Physical Society, and to about 100 other scientific men selected from the list of the Royal Society:—

"DEAR SIR,—The Physical Society of London has appointed a Committee, consisting of the PRESIDENT Prof. G. C. FOSTER, Prof. W. G. ADAMS, and Dr. ATKINSON, to gather information and report upon a proposal for issuing to its Members translations from foreign languages of important contributions to Physical Science.

"It is thought that the Society might with advantage devote some portion of its funds to supplying its Members in this way with Papers which might not otherwise be easily accessible to them.

"It is not proposed that in the choice of Papers for translation the Committee should necessarily be limited to contemporary physical literature; but that, in addition to recent Papers distinguished for the novelty and importance of the results recorded in them, whether experimental or theoretical, or for the excellence of the methods described, attention should also be given to Memoirs, irrespective of the date of their publication, which have exerted a prominent and lasting influence on the development of Physics. Selections from Textbooks, or other systematic works, in which some important subject is exceptionally well treated, might also be occasionally included.

"The Translations would be printed uniformly with the Proceedings of the Society, but would be paged separately, and, if the experiment were successful, would ultimately result in one or more volumes similar to 'Taylor's Scientific Memoirs.' The extent to which the scheme may be carried out will, however, naturally depend very greatly upon the amount of support it may receive.

"The Committee would be glad to be favoured with your opinion as to the utility of this undertaking, and more especially with any suggestions as to suitable materials for their selection.

"Please address any reply to Dr. Atkinson, Portesbery Hill, Camberley, Farnborough Station.

"We are,

"Yours faithfully,

"G. C. Foster.
"W. G. Adams.
"E. Atkinson.

"November 1877.

"Up to the present date about twenty replies have been received; with few exceptions they express decided approval of the general scheme indicated in the circular, and we have received several offers of pecuniary assistance towards carrying it out.

"The only decided objection that has been raised is one based on the idea that the scheme will not pay, and that any funds which the Society can spare for such a purpose would be better spent in promoting the acquisition of new knowledge by paying for original research. It may be replied to this that the scheme is not put forth as one likely to be self-supporting, but rather as a legitimate and useful object on which to spend some portion of the Society's funds; and that any money which the Society could devote to purposes of research would be a very insignificant addition to the funds already available for this purpose from other sources.

"Considering the replies as a whole, the Committee feel fully justified in recommending the Council to proceed with the scheme; but the precise form which it should assume is obviously a matter calling for careful consideration.

"Some of those who have sent the most detailed replies to the circular have suggested undertakings on the part of the Society which, if they could be properly carried out, would unquestionably be of high value; but none of these suggestions appear to the Committee to be as practicable as the plan indicated in the circular.

"For example, it has been proposed that the Society should undertake the preparation and publication of a series of Tables of Physical Constants. Such a work would undoubtedly be of great value if prepared with sufficient care and knowledge, and on a sufficiently comprehensive scale. But it would require ampler funds than are at the disposal of the Society, at any rate for the present, and would involve a greater amount of personal labour and supervision than the Society can command for such a purpose.

"It has also been suggested that the Society should publish exhaustive digests of the work that has been done in connexion with special Physical Problems—such, for instance, as the determination of the velocity of sound, or of the mechanical equivalent of heat, or of the absolute unit of electrical resistance. In this case, again, the Committee, while fully recognizing the great utility which work of the kind proposed would possess, hardly see how it could be efficiently carried out otherwise than as an individual literary effort, which the Society would not have any special power of furthering.

"The plan of action suggested in the circular does not seem to the Committee to be open to these objections to the same degree; and an important point in its favour is the ease with which the scale of operations could be adjusted to the funds which the Society may from time to time be able to devote to this purpose.

"The Treasurer thinks that with its present number of Members the Society might under ordinary circumstances afford to spend about £50 a year in this way. The Committee estimate that for this sum from six to eight sheets of matter might be issued to the Members. It is probable, however, that owing to the considerable outlay incurred for registering the Society, and to the cost of reprinting Sir Charles Wheatstone's papers, the Society may not be in a position to spend much this year. But it must be remembered that these are not recurring expenses."

The Council propose to take action, in general accordance with the above recommendations, at as early a date as may be practicable.

On the 28th of April the Committee appointed to take measures for the legal Incorporation of the Society reported progress; and on the 9th of June a Special General Meeting was held to consider the changes in the Bye-Laws rendered necessary by the requirements of the Board of Trade. On the 23rd of the same month the amended Bye-Laws were finally approved by the Society. The papers have since been forwarded to the Board of Trade, and have been accepted by that Department without change, a result which the Council cannot but feel is in no small measure due to the valuable suggestions and carefully considered criticisms of two Members of the Society—Mr. CHANNELL LAW and Mr. FRANK CRISP.

The Board of Trade has recently granted to the Society a Certificate of Incorporation; and this General Meeting is held, as the law directs, within four months of the Registration of the Society.

The Council need hardly recall the advantages which accrue from Registration; but it would again point out that if this important step had not been taken the liability of the Members would have been unlimited, and the Society would have been unable to hold property or to recover debts.

The question of altering the time of meeting has again been anxiously discussed by the Council; and during the present year a formal opportunity will be afforded to each of the Members of expressing an opinion as to the desirability of a change.

The Council has determined to form the nucleus of a Library by expending a certain sum annually in the purchase of periodicals, and donations of books are invited. The thanks of the Society are already due to Prof. GUTHRIE for copies of the works of Boyle and of Bacon, and to Prof. REINOLD for a copy of Newton's 'Principia.'

Several foreign and other publications have also been received during the past year, and the thanks of the Society have been offered to the respective donors. Among these may be mentioned one from our distinguished Honorary Member M. CORNU, namely, a volume of the 'Annuaire de l'Observatoire de Paris,' containing a detailed account of his recent remarkable experiments for the determination of the velocity of light.

Last year the Council determined to put in force the section of the Bye-Laws which relates to Honorary Members. Although the youthfulness of the Society caused the Council to hesitate for a time before taking this step, all were convinced that the two distinguished men who were elected last year would appreciate close relations with us, as both had shown their sympathy by reading papers at our Meetings. With regard to the two illustrious physicists whose names are submitted to you to day, the Council could not but feel that they might seek alliance with men to whom Honorary Membership is the only tribute of respect we are able as a body to offer.

The Council propose to avail themselves at an early date of their power to recommend, as an ex-officio Member of the Society, the President of the Physical Society of Paris.

Our grateful thanks are due to the Lords of the Committee of Council of Education not only, as heretofore, for permission to hold our Meetings in the Science Schools, but also for the loan of the Theatre of the South Kensington Museum on the occasion of Prof. Graham Bell's lecture. The application for the use of the Theatre was made on our behalf by Major Festing, R.E., to whom, as well as to the officers of the Museum, we are indebted for the excellent arrangements which contributed so largely to the success of the meeting.

The Treasurer presented the audited Balance-sheet, and the Society then proceeded to the election of the Council and Officers for the ensuing year, and for Honorary Members. Prof. S. P. THOMPSON and Mr. W. CONRAD COOKE were appointed Scrutators. The following gentlemen were declared duly elected:—

President.—Prof. W. G. ADAMS, M.A., F.R.S.

Vice-Presidents.—Dr. J. H. GLADSTONE, F.R.S.; Prof. G. C. FOSTER, F.R.S.; Prof. R. B. CLIFTON, M.A., F.R.S.; W. SPOTTISWOODE, LL.D., F.R.S.; W. H. STONE, M.B., F.R.C.P.; Sir WILLIAM THOMSON, LL.D., F.R.S.

Secretaries.—Prof. A. W. REINOLD, M.A.; W. CHANDLER ROBERTS, F.R.S.

Treasurer.—Dr. E. ATKINSON.

Demonstrator.—Prof. F. GUTHRIE, Ph.D., F.R.S.

Other Members of Council.—Capt. W. de W. ABNEY, R.E., F.R.S.; Prof. W. F. BARRETT, F.R.S.E.; Major E. R. FESTING, R.E.;

W. HUGGINS, D.C.L., F.R.S.; Prof. A. B. W. KENNEDY, C.E.; O. J. LODGE, D.Sc.; Prof. H. M'LEOD; The Earl of ROSSE, D.C.L., F.R.S.; Prof. W. C. UNWIN, B.Sc.; R. WORMELL, D.Sc.

Honorary Members.—Prof. HERMANN LUDWIG FERDINAND HELMHOLTZ; Prof. WILHELM EDUARD WEBER.

After the names had been announced from the Chair, votes of thanks were proposed:—to the PRESIDENT; to the Lords of the Committee of Council on Education; to the DEMONSTRATOR, TREASURER, and SECRETARIES.

THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM DECEMBER 31ST, 1876, TO DECEMBER 31ST, 1877.

Dr.	£	*s.*	*d.*	£	*s.*	*d.*
Balance in Bank December 31st				44	4	1
„ due by Treasurer				22	19	11
Entrance-Fees				25	0	0
Subscriptions for 1875				3	0	0
„ 1876				10	0	0
„ 1877				106	0	0
„ 1878				5	0	0
„ 1879				1	0	0
Compositions				120	0	0
Dividends on £400 4 per cent. Furness Debenture Stock, less Income Tax, 4*s.*				15	16	0
Dividends on £200 5 per cent. Midland Preference Stock, less Income Tax, 2*s.* 6*d.*				9	17	6
Sales of Everett's C.G.S.				20	14	0
Balance due to Treasurer				6	10	3
				£390	1	9

Cr.	£	*s.*	*d.*	£	*s.*	*d.*
Purchase of £100 5 per cent. Midland Preference Stock				123	7	3
Deed Box				1	0	1
Reports of Meetings				16	2	0
Messrs. Taylor and Francis:—						
Printing Proceedings &c., part ii. vol. ii.				38	10	6
„ „ part iii. vol. ii.				19	12	6
Separate copies				3	14	6
Postage and addressing				1	14	6
Miscellaneous Printing				17	6	2
Mr. Richardson, of Greenwich:—						
Miscellaneous Printing				1	16	0
Chapman: Attendance at Meetings	3	15	0			
Incidental Expenses	1	5	3			
				5	0	3
Petty Cash:—						
Mr. Roberts	1	3	0			
Mr. Reinold	2	17	0			
Dr. Atkinson	1	10	1			
				5	10	1
Loss on Cheque				0	0	7
India-rubber Company for expenses of Prof. Bell's Lectures				1	19	0
Balance in Bank				154	8	4
				£390	1	9

We have examined the above Account, and find that there is due to the Treasurer an amount of Six Pounds, Ten Shillings, and Threepence.

London, January 28th, 1878.

ROBT. J. LECKY,
CARLTON J. LAMBERT. } *Auditors.*

PROPERTY ACCOUNT. PHYSICAL SOCIETY.

ASSETS.	£	s.	d.	LIABILITIES.	£	s.	d.
Subscriptions due	43	0	0	Expenses of Registration	75	0	0
£400 4 per cent. Debenture Stock Furness Railway at 103	412	0	0	Expenses of the Reprint of Sir C. Wheatstone's papers	200	0	0
£300 5 per cent. Preference Stock Midland Railway at 123	369	0	0	Subscriptions in advance	6	0	0
Stock of Everett's C.G.S.	10	0	0	Due to Treasurer	6	10	3
Cash in Bank	154	8	4	Balance	700	18	1
	£988	8	4		£988	8	4

We have examined the above Account, and find that there was a balance of Seven Hundred Pounds, Eighteen Shillings, and One Penny in favour of the Society on the 31st of December, 1877.

London, January 28th, 1878.

ROBT. J. LECKY,
CARLTON J. LAMBERT. } *Auditors.*